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FEATURED REVIEW

VIEWPOINTS ON TRANSPORT PHENOMENA

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When our textbook [Bird, Stewart, and Lightfoot, 1960--hereinafter referred to as BSL] was published there was a general feeling in the profession that the book was overly theoretical and that little or ever serious use would be made of the equations of change. Because of the rapid development of computers and numerical methods in the intervening time, however, it is now possible to take a more fundamental viewpoint in the solution of certain classes of problems. As a result, the subject of transport phenomena is being increasingly used, not only in chemical engineering but in a variety of scientific and engineering disciplines.

Through the years, the viewpoints of the authors of the above-mentioned book have evolved, and we have gradually introduced new ideas into the teaching program at the University of Wisconsin. This review contains some topics not contained in BSL, as well as some material from BSL presented in a different way. Also a number of newer references are cited. Perhaps this review will be helpful to students and teachers.

For the most part the notation of BSL will be used here. In writing dot, double-dot, and cross products, we use parentheses ( ) to indicate operations that yield a scalar, brackets [ ] for those that yield a vector, and braces { } for those that yield a tensor. These enclosures further serve to show which quantities are being operated on by the ∇-operator. For example, the quantity $[\nabla\cdot\rho\mathbf{vv}]$ is a vector, and it is understood that the ∇-operator involves differentiation of all three symbols to the right of it. Similarly $(\boldsymbol{\pi}:\nabla\mathbf{v})$ and $(\nabla\cdot\rho\hat{U}\mathbf{v})$ are operations that result in scalars. Since the above rules apply only if dot or cross operations are involved, we may write either $\nabla\mathbf{v}$ or $(\nabla\mathbf{v})$, and $\mathbf{v}+\mathbf{w}$ may be written either as $(\mathbf{v}+\mathbf{w})$. or as $[\mathbf{v}+\mathbf{w}]$. Vectors are bold-face Roman letters, and tensors are bold-face Greek symbols. The unit tensor is $\boldsymbol{\delta}$ with components δ_{ij} (the Kronecker delta) , and the unit vectors in the three coordinate directions are indicated by bold-face deltas with the appropriate subscript: $\boldsymbol{\delta}_x$, $\boldsymbol{\delta}_y$, $\boldsymbol{\delta}_z$. The tensor $\boldsymbol{\varepsilon}$ is a third-order tensor, with components $\varepsilon_{ijk}=\frac{1}{2}(i-j)(j-k)(k-i)$. In equations that are written for multicomponent mixtures the various chemical species are indicated with Greek subscripts α, β, ... running from 1 to N. In equations written specifically for binary mixtures, the Roman subscripts A and B are used to designate the two chemical species. A circumflex (^) over a symbol means that it is a quantity "per unit mass".

The subject of transport phenomena makes use of the conservation laws of physics: the conservation of mass, momentum, angular momentum, and energy. These laws are taken over without question. It is worth noting that the law of conservation of energy may be derived from the homogeneity of time, the law of conservation of momentum from the homogeneity of space, and the law of angular momentum from the isotropy of space [Landau and Lifshitz, 1960, Chapter 2; Callen, 1985, §21-3].

These conservation principles may be applied to molecular collisions at the *molecular level* (in the development of kinetic theory), to an infinitesimal region within a fluid at the *microscopic level* (in the continuum development of the equations of change), and to large pieces of equipment at the *macroscopic level* (in the development of the macroscopic balances). However, at each level it is necessary to invoke some empiricisms. At the molecular level, we have to postulate a form for the intermolecular potential energy; at the microscopic level, we need expressions for the fluxes in terms of the transport properties, and at the macroscopic level, we need empirical correlations for the transfer coefficients in terms of the various relevant dimensionless groups characterizing the system.

It is also possible to speak of a *mesoscopic level* in which a multiphase system is treated as a hypothetical continuum. For example, a suspension of particles can be treated as a fictitious fluid with a prescribed viscosity (or other rheological properties). A solid containing inclusions of a second solid phase can be treated as a fictitious solid with an effective thermal conductivity. The flow through a packed bed or porous medium can be described by some kind of spatially smoothed equation such as Darcy's law. We do not enter in to a discussion of such methods of description here [see Brenner and Edwards, 1993, for a thorough presentation].

1. THE MOLECULAR VIEWPOINT

We begin by writing down the conservation laws for molecules participating in binary collisions. Then we show how this information is used in generating the equations of change from the Boltzmann equation for dilute monatomic gas mixtures. It is seen that by-products of this derivation are the formal molecular expressions for the fluxes of mass, momentum, and energy. The derivation of the kinetic theory expressions

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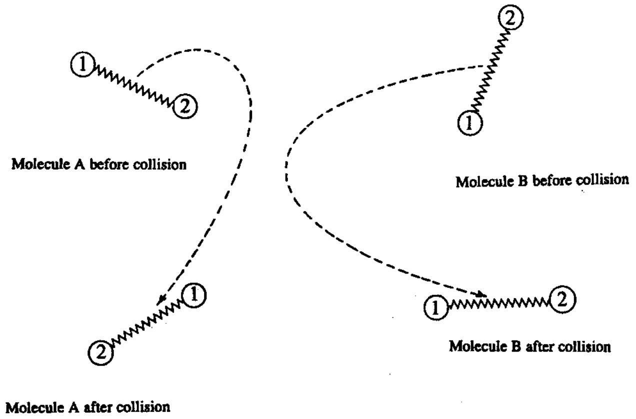
for the transport properties for dilute monatomic gas mixtures is then discussed. Finally, the molecular theory of polymeric fluids is described.

1-1. Conservation Laws in Molecular Collisions

A rigorous description of molecular motions and collisions requires quantum mechanics; however, classical mechanics is usually adequate for use in kinetic theory, except for the lightest of molecules (He and H_2) at very low temperatures. In Fig. 1 we depict a collision between two homonuclear diatomic molecules, A and B, in a dilute gas, in the absence of chemical reactions; we also show the coordinate system used to describe the locations of the two atoms, "1" and "2", in the molecule A by means of position vectors with respect to an arbitrarily chosen origin.

We want to obtain relations between certain quantities before and after a collision. By "before a collision" we mean that the two molecules destined to collide are sufficiently far from one another, so that there is no intermolecular force felt between the molecules; similarly "after the collision" means that the molecules have traveled far enough following their encounter so that the intermolecular forces are no longer felt. Quantities after the collision are designated by primes.

(a) A collision between homonuclear diatomic molecules



(b) Position vectors for the atoms in molecule A

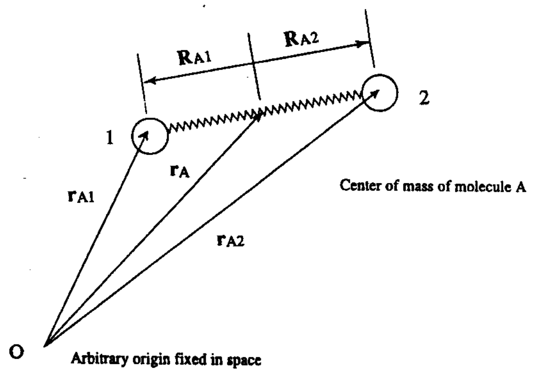


Fig. 1. A collision between two homonuclear diatomic molecules, in which mass, momentum, angular momentum, and energy are conserved. Quantities after a collision have primes on them.

(a) According to the *law of conservation of mass,* the total mass of the molecules entering and leaving the collision must be equal:

$$\mathrm{m}_A + \mathrm{m}_B = \mathrm{m}'_A + \mathrm{m}'_B. \tag{1}$$

Here m_A and m_B are the masses of molecules A and B. Since there are no chemical reactions, the masses of the individual species will also be conserved, so that

$$\mathrm{m}_A = \mathrm{m}'_A, \text{ and } \mathrm{m}_B = \mathrm{m}'_B. \tag{2}$$

(b) According to the *law of conservation of momentum* the total momentum of the molecules that are about collide must equal that of the molecules after the collision, so that

$$\begin{aligned}\mathrm{m}_{A1}\dot{\mathbf{r}}_{A1} + \mathrm{m}_{A2}\dot{\mathbf{r}}_{A2} + \mathrm{m}_{B1}\dot{\mathbf{r}}_{B1} + \mathrm{m}_{B2}\dot{\mathbf{r}}_{B2} &= \\ \mathrm{m}'_{A1}\dot{\mathbf{r}}'_{A1} + \mathrm{m}'_{A2}\dot{\mathbf{r}}'_{A2} + \mathrm{m}'_{B1}\dot{\mathbf{r}}'_{B1} + \mathrm{m}'_{B2}\dot{\mathbf{r}}'_{B2}&,\end{aligned} \tag{3}$$

in which $\mathbf{r}_{A1}$ is the position vector for atom "1" of molecule A, and $\dot{\mathbf{r}}_{A1}$ is its velocity. If we switch to the molecule center-of-mass position vector $\mathbf{r}_A$ and the relative position vectors $\mathbf{R}_{A1}$ and $\mathbf{R}_{A2}$, and then recognize that $\mathbf{R}_{A2} = -\mathbf{R}_{A1}$ (with a similar relation being true for the corresponding velocities), we get

$$\mathrm{m}_A\dot{\mathbf{r}}_A + \mathrm{m}_B\dot{\mathbf{r}}_B = \mathrm{m}_A\dot{\mathbf{r}}'_A + \mathrm{m}_B\dot{\mathbf{r}}'_B. \tag{4}$$

Here we have also used the fact that, for homonuclear diatomic molecules, $\mathrm{m}_{A1}=\mathrm{m}_{A2}=\frac{1}{2}\mathrm{m}_A$.

(c) According to the *law of conservation of energy,* the energy of the colliding pair of molecules must be the same before and after the collision. The energy of a molecule consists of the sum of the kinetic energies of the atoms and the interatomic potential energy, ϕ_A, which describes the force of the chemical bond that joins the two atoms "1" and "2" of molecule A, and is a function of $|\mathbf{r}_{A2}-\mathbf{r}_{A1}|$. Therefore energy conservation leads to

$$\begin{aligned}\left(\frac{1}{2}\mathrm{m}_{A1}\dot{\mathbf{r}}_{A1}^2 + \frac{1}{2}\mathrm{m}_{A2}\dot{\mathbf{r}}_{A2}^2 + \phi_A\right) + \left(\frac{1}{2}\mathrm{m}_{B1}\dot{\mathbf{r}}_{B1}^2 + \frac{1}{2}\mathrm{m}_{B2}\dot{\mathbf{r}}_{B2}^2 + \phi_B\right) &= \\ \left(\frac{1}{2}\mathrm{m}'_{A1}\dot{\mathbf{r}}'^2_{A1} + \frac{1}{2}\mathrm{m}'_{A2}\dot{\mathbf{r}}'^2_{A2} + \phi'_A\right) + \left(\frac{1}{2}\mathrm{m}'_{B1}\dot{\mathbf{r}}'^2_{B1} + \frac{1}{2}\mathrm{m}'_{B2}\dot{\mathbf{r}}'^2_{B2} + \phi'_B\right)&.\end{aligned} \tag{5}$$

By switching to the coordinates for the center of mass and the relative coordinates (and the corresponding velocities) we get

$$\begin{aligned}\left(\frac{1}{2}\mathrm{m}_A\dot{\mathbf{r}}_A^2 + \mathrm{u}_A\right) + \left(\frac{1}{2}\mathrm{m}_B\dot{\mathbf{r}}_B^2 + \mathrm{u}_B\right) &= \\ \left(\frac{1}{2}\mathrm{m}_A\dot{\mathbf{r}}'^2_A + \mathrm{u}'_A\right) + \left(\frac{1}{2}\mathrm{m}_B\dot{\mathbf{r}}'^2_B + \mathrm{u}'_B\right)&,\end{aligned} \tag{6}$$

in which $\mathrm{u}_A=\sum_k \frac{1}{2}\mathrm{m}_{Ak}\dot{\mathbf{R}}_{Ak}^2 + \phi_A$ is the sum of the kinetic energies of the atoms referred to the center of mass of molecule A, and the interatomic potential energy of molecule A. Thus we split up the energy of each molecule into its kinetic energy with respect to fixed coordinates, and the internal energy of the molecule (which includes the vibrational, rotational, and interatomic potential energies).

(d) Finally, the *law of conservation of angular momentum* can be applied to a collision to give

$$\begin{aligned}&([\mathbf{r}_{A1}\times \mathrm{m}_{A1}\dot{\mathbf{r}}_{A1}]+[\mathbf{r}_{A2}\times \mathrm{m}_{A2}\dot{\mathbf{r}}_{A2}])\\ &\quad+([\mathbf{r}_{B1}\times \mathrm{m}_{B1}\dot{\mathbf{r}}_{B1}]+[\mathbf{r}_{B2}\times \mathrm{m}_{B2}\dot{\mathbf{r}}_{B2}])\\ &=([\mathbf{r}'_{A1}\times \mathrm{m}'_{A1}\dot{\mathbf{r}}'_{A1}]+[\mathbf{r}'_{A2}\times \mathrm{m}'_{A2}\dot{\mathbf{r}}'_{A2}])\\ &\quad+([\mathbf{r}'_{B1}\times \mathrm{m}'_{B1}\dot{\mathbf{r}}'_{B1}]+[\mathbf{r}'_{B2}\times \mathrm{m}'_{B2}\dot{\mathbf{r}}'_{B2}]). \qquad (7)\end{aligned}$$

Next we introduce center-of-mass and relative coordinates and velocities and obtain:

$$\begin{aligned}&([\mathbf{r}_A\times \mathrm{m}_A\dot{\mathbf{r}}_A]+\boldsymbol{l}_A)+([\mathbf{r}_B\times \mathrm{m}_B\dot{\mathbf{r}}_B]+\boldsymbol{l}_B)=\\ &\qquad([\mathbf{r}'_A\times \mathrm{m}_A\dot{\mathbf{r}}'_A]+\boldsymbol{l}'_A)+([\mathbf{r}'_B\times \mathrm{m}_B\dot{\mathbf{r}}'_B]+\boldsymbol{l}'_B), \qquad (8)\end{aligned}$$

in which $\boldsymbol{l}_A=[\mathbf{R}_{A1}\times \mathrm{m}_{A1}\dot{\mathbf{R}}_{A1}]+[\mathbf{R}_{A2}\times \mathrm{m}_{A2}\dot{\mathbf{R}}_{A2}]$ is the internal angular momentum of molecule A.

The conservation laws for the collisions of monatomic molecules can be obtained from the results above as follows: Eqs. (1), (2), and (4) are directly applicable; Eq. (6) is applicable if the internal energy contributions are omitted; and Eq. (8) may be used if the internal angular momentum terms are discarded [see §1.5 of Hirschfelder et al., 1964, for a discussion of collisions between monatomic molecules].

1-2. Fluxes as Integrals over the Distribution Function

In applying kinetic theory (nonequilibrium statistical mechanics) to any kind of system, it is necessary to derive some kind of equation for a distribution function and to know how to solve it. For a dilute non-reacting monatomic gas mixture [Chapman and Cowling, 1970, Chapter 3; Hirschfelder et al., 1964, Chapter 7; Lifshitz and Pitaevskii, 1981, Chapter 1], the relevant equation is the *Boltzmann equation* for $\mathrm{f}_\alpha(\mathbf{r}, \dot{\mathbf{r}}_\alpha, \mathrm{t})$, which is the probability density that at position $\mathbf{r}$, and time t, a molecule of species α will have a velocity $\dot{\mathbf{r}}_\alpha$:

$$\frac{\partial \mathrm{f}_\alpha}{\partial \mathrm{t}}+\left(\dot{\mathbf{r}}_\alpha\cdot\frac{\partial \mathrm{f}_\alpha}{\partial \mathbf{r}}\right)+\left(\mathbf{g}_\alpha\cdot\frac{\partial \mathrm{f}_\alpha}{\partial \dot{\mathbf{r}}_\alpha}\right)=\mathrm{J}_\alpha \qquad (9)$$

Here $\mathbf{g}_\alpha$ is the force per unit mass acting on a molecule of species α, and J_α is a very complicated multiple integral term accounting for the change in the distribution function resulting from molecular collisions; this term involves the intermolecular potential energy function and the details of the collision dynamics. The distribution function is normalized to the number density of species α: $\int \mathrm{f}_\alpha(\mathbf{r}, \dot{\mathbf{r}}_\alpha, \mathrm{t})d\dot{\mathbf{r}}_\alpha=\mathrm{n}_\alpha$.

Recently it has been shown [Curtiss, 1992a, b, c] that the Boltzmann equation in Eq. (9) is incomplete in that it does not account for the existence of "bound pairs" of molecules, that is, pairs of molecules that orbit around one other; Curtiss has shown how to correct the equation and to use the appropriately modified equation to compute the transport properties. The effect of this modification is important, however, only at very low temperatures.

When Eq. (9) is multiplied by a molecular property ψ_α and then integrated over all molecular velocities, the *general equation of change* is obtained:

$$\frac{\partial(\mathrm{n}_\alpha\overline{\psi}_\alpha)}{\partial \mathrm{t}}+\left(\frac{\partial}{\partial \mathbf{r}}\cdot \mathrm{n}_\alpha\overline{\dot{\mathbf{r}}_\alpha\psi_\alpha}\right)-\mathrm{n}_\alpha\left[\overline{\frac{\partial \psi_\alpha}{\partial \mathrm{t}}}+\overline{\left(\dot{\mathbf{r}}_\alpha\cdot\frac{\partial \psi_\alpha}{\partial \mathbf{r}}\right)}+\left(\mathbf{g}_\alpha\cdot\overline{\frac{\partial \psi_\alpha}{\partial \dot{\mathbf{r}}_\alpha}}\right)\right]=\int \mathrm{J}_\alpha\psi_\alpha d\dot{\mathbf{r}}_\alpha, \qquad (10)$$

in which the overbar indicates an average value defined as follows:

$$\overline{\psi}_\alpha(\mathbf{r}, \mathrm{t})=(1/\mathrm{n}_\alpha)\int \psi_\alpha(\dot{\mathbf{r}}_\alpha)\mathrm{f}_\alpha(\mathbf{r}, \dot{\mathbf{r}}_\alpha, \mathrm{t})d\dot{\mathbf{r}}_\alpha \qquad (11)$$

Next, we let ψ_α be successively m_α, the three components of $\mathrm{m}_\alpha(\dot{\mathbf{r}}_\alpha-\mathbf{v})$, and $\frac{1}{2}\mathrm{m}_\alpha(\dot{\mathbf{r}}_\alpha-\mathbf{v})^2$, in which $\mathbf{v}$ is the mass-average velocity of the fluid mixture. These three choices for ψ_α involve conserved quantities: mass, momentum, and energy; for such quantities the collision term on the right side of Eq. (10) can be shown to vanish [Hirschfelder, et al., 1964, §7.2], and the *equations of change* for mass, momentum, and energy are obtained:

$$\frac{\partial}{\partial \mathrm{t}}\rho_\alpha=-(\nabla\cdot\rho_\alpha\mathbf{v})-(\nabla\cdot\mathbf{j}_\alpha), \qquad (12)$$

$$\frac{\partial}{\partial \mathrm{t}}\rho\mathbf{v}=-[\nabla\cdot\rho\mathbf{v}\mathbf{v}]-[\nabla\cdot\boldsymbol{\pi}]+\Sigma_\alpha\rho_\alpha\mathbf{g}_\alpha, \qquad (13)$$

$$\begin{aligned}\frac{\partial}{\partial \mathrm{t}}\left(\frac{1}{2}\rho v^2+\frac{3}{2}\mathrm{nkT}\right)=&-\left(\nabla\cdot\left(\frac{1}{2}\rho v^2+\frac{3}{2}\mathrm{nkT}\right)\mathbf{v}\right)-(\nabla\cdot\mathbf{q})\\ &-(\nabla\cdot[\boldsymbol{\pi}\cdot\mathbf{v}])+\Sigma_\alpha((\mathbf{j}_\alpha+\rho_\alpha\mathbf{v})\cdot\mathbf{g}_\alpha), \qquad (14)\end{aligned}$$

in which the *molecular fluxes* $\mathbf{j}_\alpha$, $\boldsymbol{\pi}$, and $\mathbf{q}$ are given as integrals over the distribution function:

$$\mathbf{j}_\alpha=\mathrm{n}_\alpha\mathrm{m}_\alpha\overline{(\dot{\mathbf{r}}_\alpha-\mathbf{v})}, \qquad (15)$$

$$\boldsymbol{\pi}=\sum_\alpha \mathrm{n}_\alpha\mathrm{m}_\alpha\overline{(\dot{\mathbf{r}}_\alpha-\mathbf{v})(\dot{\mathbf{r}}_\alpha-\mathbf{v})}, \qquad (16)$$

$$\mathbf{q}=\sum_\alpha\frac{1}{2}\mathrm{n}_\alpha\mathrm{m}_\alpha\overline{(\dot{\mathbf{r}}_\alpha-\mathbf{v})^2(\dot{\mathbf{r}}_\alpha-\mathbf{v})}. \qquad (17)$$

Note the similarity in the structures of these *molecular fluxes* and those for the *convective fluxes* $\rho_\alpha\mathbf{v}$, $\rho\mathbf{v}\mathbf{v}$, and $\frac{1}{2}\rho v^2\,\mathbf{v}$ appearing in the equations of change above.

The above discussion illustrates how one can begin at the molecular level and obtain the equations of change, Eqs. (12) to (14), and at the same time generate expressions for the molecular fluxes in terms of integrals involving a distribution function, Eqs. (15) to (17). This same technique has been used for monatomic liquids [Irving and Kirkwood, 1950; Bearman and Kirkwood, 1958] and for polymeric liquids [Curtiss and Bird, 1996a, b, 1997]. For liquids the kinetic theory is much more complicated because of the diverse mechanisms for transport and because it is necessary to invoke distribution functions for pairs of molecules, about which relatively little is known at present. Nonetheless, the formal theories have been developed, and these can be used with some confidence for further developments in the theory of liquids.

1-3. Molecular Expressions for the Transport Properties

To evaluate the fluxes for low-density gas mixtures an explicit expression for the distribution function $\mathrm{f}_\alpha(\mathbf{r}, \dot{\mathbf{r}}_\alpha, \mathrm{t})$ is needed, and this is obtained by solving the Boltzmann equation.

The solution of this complicated integrodifferential equation was one of the great triumphs of theoretical physics in the first part of the twentieth century, and discussions of the details are readily available [Chapman and Cowling, 1970; Hirschfelder et al., 1964]. For a system at equilibrium the solution of the equation is just the well-known Maxwell-Boltzmann distribution.

For nonequilibrium systems one expands the distribution function in terms of the gradients of concentration, velocity, and temperature. In this way expressions are obtained for the coefficients associated with each of these gradients, that is, the *transport properties*. The formal expressions were worked out for multicomponent mixtures in mid-century [Curtiss and Hirschfelder, 1949], and shortly thereafter extensive tables were prepared for estimating the transport properties by using the Lennard-Jones 6-12 intermolecular potential, which accounts for the attractive and repulsive forces between pairs of molecules [Hirschfelder et al., 1964, §1.3]:

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{18}$$

Here $\phi(r)$ is the intermolecular potential energy as a function of the intermolecular separation r. The parameter ε is the maximum energy of attraction for the pair of molecules, and σ is the distance at which the potential energy is zero--the "collision diameter".

The simplest formulas for the transport properties are those for a pure dilute gas; in the lowest approximation (good enough for most purposes) these are:

$$\text{Self-diffusivity: } \mathcal{D} = \frac{3}{8}\left(\frac{\sqrt{\pi mkT}}{\pi\sigma^2\Omega_{\mathcal{D}}}\right)\left(\frac{1}{\rho}\right) = \frac{3}{8}\left(\frac{\sqrt{\pi k^3T^3/m}}{p\pi\sigma^2\Omega_{\mathcal{D}}}\right), \tag{19}$$

$$\text{Viscosity: } \eta = \frac{5}{16}\left(\frac{\sqrt{\pi mkT}}{\pi\sigma^2\Omega_{\mu}}\right), \tag{20}$$

$$\text{Thermal conductivity: } k = \frac{75}{64}\left(\frac{\sqrt{\pi mkT}}{\pi\sigma^2\Omega_{\mu}}\right)\left(\frac{k}{m}\right) = \frac{15}{4}\left(\frac{k}{m}\right)\mu. \tag{21}$$

Here m is the mass of a molecule, T the absolute temperature, k Boltzmann's constant. The quantities $\Omega_{\mathcal{D}}$ and Ω_μ are functions of the dimensionless temperature kT/ε; the most up-to-date tabulation of these functions is that based on Curtiss's modified Boltzmann equation [Curtiss, 1992c]. Similar formulas are available for the properties of multicomponent mixtures, as well as for the coefficient of thermal diffusion [Hirschfelder et al., 1964, Chapter 8]. From these formulas we see that viscosity and thermal conductivity are closely related and independent of the pressure; the self-diffusivity is inversely proportional to the pressure and has a stronger temperature dependence than the other two properties. The formulas for viscosity and diffusivity, although derived for a monatomic gas, can be applied to a polyatomic gas; however, the thermal conductivity formula has to be modified appreciably for polyatomic gases [Hirschfelder et al., 1964, Chapter 8].

For teaching purposes, the "linearized Boltzmann equation" (also called the "Krooked Boltzmann equation") can be recommended [Bhatnagar et al., 1954; Gross and Jackson, 1959; see also Vincenti and Kruger, 1965, Chapter X; Ferziger and Kaper, 1972, Chapter 15]. This equation can be solved relatively easily, and beginners can get a good understanding of the physical processes involved.

Rigorous kinetic theories for dilute polyatomic gases, dense monatomic gases, and monatomic liquids have been developed during the last several decades, but these are extremely complex, and progress has been slow.

1-4. Polymeric Liquids

Polymer molecules are characterized by their enormous diversity (chain molecules, ring molecules, star-shaped molecules, and many more) and their very high molecular weight. Whereas gas molecules can be satisfactorily idealized as mass points, in the statistical mechanics of polymer molecules it is essential to take into account the extension of the molecules in space and their many internal degrees of freedom. Most of the kinetic theories developed so far have been for "bead-spring" models, in which the polymers are depicted as collections of mass points ("beads") interconnected by "springs", with the connectivity so chosen that the molecular architecture is described in whatever detail is deemed essential. To date much effort has been expended on "dumbbell" models--two beads connected by one spring; despite their simplicity, they describe the salient features of polymer molecules needed for describing rheological properties: orientability and extensibility.

In developing the kinetic theory for the bead-spring models, it is necessary to find the differential equation from which the one-molecule distribution function may be obtained. Because of the large number of degrees of freedom the equation for the distribution function will involve many variables and will hence be impossible to solve (except for the dumbbell models and a few others). For polymeric liquids it will also be necessary to find the two-molecule distribution function, and virtually nothing is known about this at present. We do, however, have formal expressions for the fluxes in terms of the one- and two-molecule distribution functions (i. e., expressions analogous to Eqs. (15) to (17)) [Curtiss and Bird, 1996a]. In Fig. 2 we show what the contributions are to the fluxes of mass, momentum, and energy as given by that theory and a pictorial description of the mechanisms for transport. With the bead-spring models some successes have been achieved in describing the rheological properties of polymers (non-Newtonian viscosity, normal stresses, complex viscosity, stress relaxation, elongational flow, etc.)[Bird, et al., 1987b]. For the simplest models it has even been possible to obtain rheological constitutive equations, that is, expressions for the stress tensor in terms of the salient kinematic tensors. Relatively little has been done on the thermal and diffusive properties [Curtiss and Bird, 1996a, b, 1997]; the kinetic theory has shown that the fluxes of mass and heat depend on the velocity gradients in the fluid, but there are almost no experimental data to support the theory.

Because of the formidable mathematical problems encountered in the use of statistical mechanics to obtain the transport properties of polymeric liquids, researchers have recent-

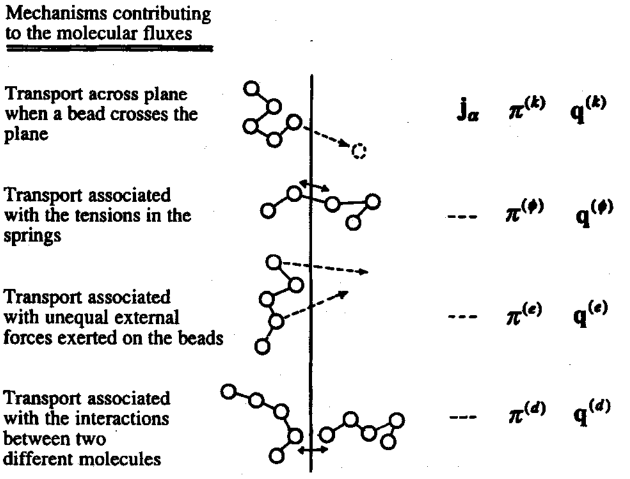


Fig. 2. Mechanisms for transport across a plane for bead-spring models of polymers.

ly turned to the use of stochastic simulations, and considerable success has been achieved by these "Brownian dynamics techniques" [Öttinger, 1996, Chapters 4-6]. Here one lets the computer follow the motions of a typical molecule exposed to velocity, temperature, or concentration gradients, and then by a statistical averaging procedure ultimately obtains the molecular fluxes in the system.

2. THE MICROSCOPIC VIEWPOINT

We now turn to a discussion of the transport phenomena equations as developed from the continuum point of view. To derive the equations of change we write conservation laws over a "control volume" within the fluid. In doing this it is necessary to account for the flux of mass, momentum, angular momentum, and energy across the surface of the control volume. These entities are transported by two mechanisms: by the motion of the fluid (*convective transport*) and by the motion of the molecules with respect to the fluid velocity (*molecular transport*).

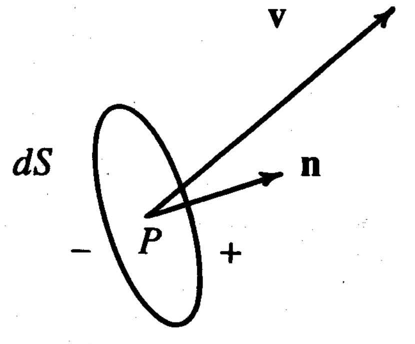


Fig. 3. The vector v is the fluid velocity vector at some point P in 3-dimensional space. The unit vector n is perpendicular to a differential surface element dS. The region on the n-vector side of the surface is referred to as the *plus* region, and the other is called the *minus* region. The component of v in the n direction is (n·v), and the volume rate of flow from the minus side to the plus side through dS is (n·v) dS.

An element of surface dS with unit normal vector **n** is shown in Fig. 3; the fluid is flowing through this surface with a velocity **v**. For a mixture, **v** is the mass-average velocity, $\mathbf{v}=\sum_\alpha \omega_\alpha \mathbf{v}_\alpha$, in which ω_α is the mass fraction of species α and $\mathbf{v}_\alpha$ is the velocity of species α. The side of the surface dS where the arrow is drawn is called the "plus side", and the other is the "minus side". The terms "plus material" and "minus material" refer to the fluid material on the two sides.

2-1. The Convective Fluxes

We have to consider the transport of both scalar and vector quantities. We use the symbol B to represent some scalar quantity per unit volume; examples of scalar quantities are: fluid density ρ (mass/volume), concentration ρ_α (mass of species α/volume), kinetic energy per unit volume $\frac{1}{2}\rho v^2=\frac{1}{2}\rho(\mathbf{v}\cdot\mathbf{v})$, internal energy per unit volume $\rho\hat{U}$, and potential energy per unit volume $\rho\hat{\Phi}$. We use the symbol **B** to represent a vector quantity per unit volume; examples of this are: linear momentum per unit volume $\rho\mathbf{v}$ and angular momentum per unit volume $[\mathbf{r}\times\rho\mathbf{v}]$.

The volume rate of flow of fluid across dS from the minus side to the plus side is $(\mathbf{n}\cdot\mathbf{v})$dS. Then the rate of flow of B (with dimensions of $(\cdots)$/volume) across dS is $(\mathbf{n}\cdot\mathbf{v})$BdS with dimensions of $(\cdots)$/time. When we divide this by dS we get $(\mathbf{n}\cdot\mathbf{v})B=(\mathbf{n}\cdot\mathbf{v}B)$, which has dimensions of $(\cdots)$/(area)(time) and which gives the rate at which the scalar quantity is being transported by convection from the minus side of the surface to the plus side of dS. The vector quantity **v**B is then referred to

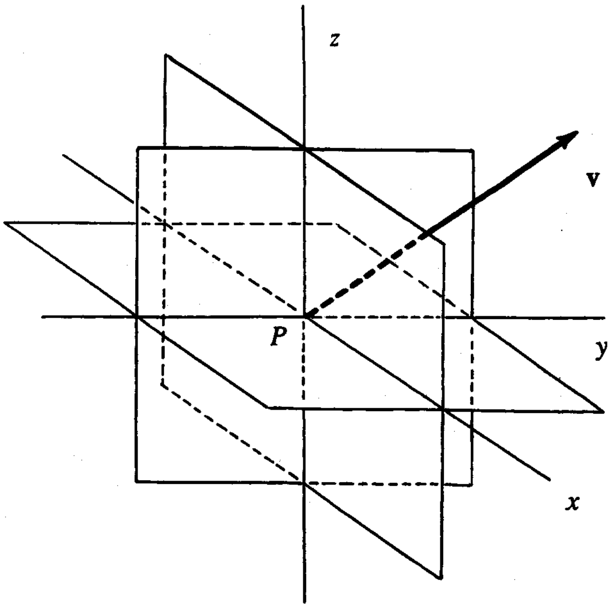


Fig. 4. Three mutually perpendicular differential surfaces, each with area dS, perpendicular to the three coordinate directions; the unit vectors in the x-, y-, and z-coordinate directions are δ_x, δ_y, and δ_z respectively. The fluid velocity is v at the point P in a three-dimensional space through which the fluid is flowing. The flux of a scalar quantity B across a plane perpendicular to the y-direction is $(\delta_y\cdot\mathbf{v}B)=v_yB$. The flux of the z-component of a vector quantity B across the plane perpendicular to the x-direction is $(\delta_x\cdot\mathbf{v}\mathbf{B}\cdot\delta_z)=(\delta_z\delta_x:\mathbf{v}\mathbf{B})=v_xB_z$.

as the "flux of B". The flux of B may also be written in terms of its components: $\mathbf{v}B=\Sigma_k \boldsymbol{\delta}_k v_k B$, where $\boldsymbol{\delta}_k$ is the unit vector in the k-th coordinate direction. If one wants to know, in Fig. 4, what the flux of a particular quantity is across a plane perpendicular to the x-direction, this is obtained by taking the dot product of the unit vector in the x-direction with the flux: $(\boldsymbol{\delta}_x \cdot \mathbf{v}B)=v_x B$. This is then called the flux of B in the x-direction. The following vector fluxes will be important:

$\rho\mathbf{v}$	the (total) mass flux,
$\rho_\alpha \mathbf{v}$	the species mass flux,
$\frac{1}{2}\rho v^2 \mathbf{v}$	the kinetic energy flux,
$\rho\hat{U}\mathbf{v}$	the internal energy flux,
$\rho\hat{\Phi}\mathbf{v}$	the potential energy flux.

For a vector quantity, the rate of flow of $\mathbf{B}$ by convection across dS is $(\mathbf{n}\cdot\mathbf{v})\mathbf{B}dS$. When this is divided by dS we get $(\mathbf{n}\cdot\mathbf{v})\mathbf{B}=[\mathbf{n}\cdot\mathbf{vB}]$, which is the rate at which the vector quantity is being transported by convection from the minus side of dS to the plus side. The tensor quantity $\mathbf{vB}$ is called the "flux of $\mathbf{B}$", and it may be displayed in terms of its components as: $\mathbf{vB}=\Sigma_j\Sigma_k \boldsymbol{\delta}_j \boldsymbol{\delta}_k v_j B_k$. If we want to know, in Fig. 4, what the flux of the y-component of $\mathbf{B}$ is across a plane perpendicular to the z-direction, this is obtained by $(\boldsymbol{\delta}_z \cdot \mathbf{vB} \cdot \boldsymbol{\delta}_y)=v_z B_y$. Note that the first subscript gives the direction of transport, and the second gives the component of the vector quantity being transported. Tensor fluxes that arise in transport phenomena are:

$\mathbf{v}(\rho\mathbf{v})=\rho\mathbf{vv}$	the momentum flux,
$\mathbf{v}[\mathbf{r}\times\rho\mathbf{v}]=\rho\mathbf{v}[\mathbf{r}\times\mathbf{v}]$	the angular-momentum flux.

The first of these tensors is symmetric and the second is not.

To summarize: the rate of flow of any scalar quantity B (or any vector quantity $\mathbf{B}$) across an element of surface dS with orientation $\mathbf{n}$ because of convective transport is obtained by dotting $\mathbf{n}$ into the vector flux $\mathbf{v}B$ (or the tensor flux $\mathbf{vB}$) and multiplying by dS. It should be emphasized that the scalar flux may be written $\mathbf{v}B$ or $B\mathbf{v}$, but that the tensor flux must in general be written $\mathbf{vB}$ and not $\mathbf{Bv}$.

2-2. The Molecular Fluxes

The molecular fluxes account for transport of mass, momentum, and energy above and beyond the convective transport by the fluid motion. In their simplest form, these fluxes are given as linear relations involving the concentration, velocity, and temperature gradients. These equations are usually associated with the names of Fick, Newton, and Fourier respectively. The flux expressions are sometimes inappropriately referred to as "laws". They are just empirical proposals, which, for a wide range of materials over wide ranges of conditions, have been found experimentally to be valid. We summarize them here [BSL, Eq. C of Table 16.2-1, Eq. 18.4-1, Eq. 18.4-2]:

$$\text{Mass Flux: } \mathbf{j}_A=-\rho\mathcal{D}_{AB}\nabla\omega_A, \tag{22}$$

$$\text{Momentum Flux: } \boldsymbol{\pi}=p\,\boldsymbol{\delta}-\mu(\nabla\mathbf{v}+(\nabla\mathbf{v})^{\dagger})+\left(\frac{2}{3}\mu-\kappa\right)(\nabla\cdot\mathbf{v})\boldsymbol{\delta}, \tag{23}$$

$$\text{Heat Flux: } \mathbf{q}=-k\nabla T+\sum_\alpha(\bar{H}_\alpha/M_\alpha)\mathbf{j}_\alpha. \tag{24}$$

In Eq. (23) the superscript "†" indicates the transpose of a tensor quantity. These expressions are incomplete, as is explained in the discussion on nonequilibrium thermodynamics in §2.5 below.

Eq. (22) is valid for binary systems only and is sometimes called "Fick's (first) law of diffusion". The quantity $\mathcal{D}_{\alpha\beta}$, with units m^2/s, is the *diffusivity* of the system A-B (A and B being two chemical species). Fick's law states that a mass flux results from a gradient in the mass fraction ω_A. The expressions for the mass fluxes in systems with N species (with N> 2) are more complicated, because each species flux depends on all the concentration gradients in the fluid, with $\frac{1}{2}N(N-1)$ diffusivities $\mathcal{D}_{\alpha\beta}$. For dilute monatomic gases the equations for multicomponent ordinary diffusion are known to be given by the *Maxwell-Stefan equations*,

$$\nabla x_\alpha=\sum_{\beta=1}^{N}\frac{x_\alpha x_\beta}{\mathcal{D}_{\alpha\beta}}\left(\frac{\mathbf{j}_\beta}{\rho_\beta}-\frac{\mathbf{j}_\alpha}{\rho_\alpha}\right),\quad \alpha=1, 2, ...N. \tag{25}$$

Here x_α is the mole fraction of species α, and ρ_α is the mass concentration of α. Equations of this form are often used, apparently with some success, for compressed gases and for liquids [Hirschfelder et al., 1964; Bird et al., 1960; Lightfoot, 1974; Taylor and Krishna, 1993]; a similar equation has also been obtained for polymeric liquids [Curtiss and Bird, 1996b].

Eq. (23) is a generalization of "Newton's law of viscosity" and the establishment of the tensorial form is discussed in many textbooks [Aris, 1962, §5.22 to §5.24; Batchelor, 1967, §3.3; Whitaker, 1968, §5.2]. It contains two coefficients: the *viscosity* μ and the *dilatational viscosity* κ (or *bulk viscosity*), both with units kg/m·s or Pa·s. The term "dynamic viscosity" should not be used for μ, since this term has a different meaning in linear viscoelasticity. Also it is misleading to refer to μ as the "shear viscosity", since, in the equation of motion, μ may arise in terms describing elongation or dilatation. The dilatational viscosity κ is zero for dilute, monatomic gases, according to the Chapman-Enskog kinetic theory [Chapman and Cowling, 1970; Hirschfelder et al., 1964]. For polyatomic gases it is not zero and is important in sound transmission [Landau and Lifshitz, 1987, Chapter VIII]. It is also important for liquids containing gas bubbles, when treating the two-phase system as an equivalent one-phase system [Batchelor, 1967, pp. 253-255]. The p in Eq. (23) is the thermodynamic pressure; that is, it is considered to be the same function of density, temperature, and composition as for the fluid at equilibrium. Note that the momentum-flux tensor for the Newtonian fluid is symmetric, so that $\pi_{jk}=\pi_{kj}$.

Eq. (24) consists of two terms. The first term (called "Fourier's law of heat conduction") states that heat is transported because of a temperature gradient, and the proportionality coefficient k is called the *thermal conductivity*, with units of W/mK. The second term describes the heat transport by diffusional processes, being the sum of products of mass fluxes and the partial specific enthalpies $(\bar{H}_\alpha/M_\alpha)$. In some high-temperature systems, one should also add to the heat-flux vector another term accounting for radiative energy transfer [Sampson, 1965; Sparrow and Cess, 1966; Pomraning, 1973].

The molecular fluxes in Eqs. (22) to (24) obey the same sign conventions as the convective fluxes. That is, $(\mathbf{n}\cdot\mathbf{j}_A)$ is the mass flux from the minus side to the plus side across a surface of unit area with normal unit vector $\mathbf{n}$, and $(\mathbf{n}\cdot\mathbf{q})$ is the heat flux across a surface of unit area in the same direction. Similarly the momentum flux is given by $[\mathbf{n}\cdot\boldsymbol{\pi}]$. This quantity may also be interpreted as the force exerted by the minus material on the plus material across a surface of unit area with normal unit vector $\mathbf{n}$. If at that surface the fluid is flowing with a velocity $\mathbf{v}$, then the rate of doing work by the minus material on the plus material will be the force times the velocity or $([\mathbf{n}\cdot\boldsymbol{\pi}]\cdot\mathbf{v})$, which may also be written as $(\mathbf{n}\cdot[\boldsymbol{\pi}\cdot\mathbf{v}])$.

The molecular fluxes may be written in component form in the same way as the convective fluxes. In particular, the momentum flux tensor is $\boldsymbol{\pi}=\sum_j\sum_k\boldsymbol{\delta}_j\boldsymbol{\delta}_k\pi_{jk}$, in which π_{jk} is the flux of k-momentum in the positive j-direction. It may also be interpreted as the force in the k-direction on a unit area perpendicular to the j-direction, this being the force exerted by the minus material on the plus material.

The notation used for the convective and molecular fluxes is summarized in Table 1. The sign conventions for the convective fluxes are generally agreed upon, as are those for the mass-flux vector and the heat-flux vector. In kinetic theory and transport phenomena it is usual to use the sign convention for $\boldsymbol{\pi}$ given above, so that all three molecular fluxes obey the same sign convention that is used for the three convective fluxes [Bird et al., 1960; Waldmann, 1958; de Groot and Mazur, 1962; Chapman and Cowling, 1970; Ferziger and Kaper, 1972; Baird and Collias, 1995]. An additional advantage is that compression is regarded as positive, in agreement with the accepted sign convention in thermodynamics [note that $\boldsymbol{\pi}$ and $p\boldsymbol{\delta}$ have the same sign in Eq. (23)]. On the other hand, in fluid dynamics and elasticity it is conventional to define a total *stress tensor* $\boldsymbol{\sigma}$ in such a way that $[\mathbf{n}\cdot\boldsymbol{\sigma}]$ is the force on a unit surface with normal unit vector $\mathbf{n}$, the force being transmitted from the plus material to the minus material. Thus $\boldsymbol{\pi}=-\boldsymbol{\sigma}$. This difference in convention causes no real problems as long as one keeps in mind the physical significance of the sign convention being used.

In solving transport phenomena problems, experimental values for the transport properties and equation of state should be used whenever possible. Data on viscosity and thermal conductivity for pure fluids can be found in a variety of handbooks, but data on mixtures are more difficult to find. Experimental data on binary diffusivities are not particularly plentiful, and those for multicomponent diffusion are quite scarce [see, for example, Landolt-Börnstein, 1952; Reid, et al., 1987; Vargaftik, 1983; Yaws, 1995; Stephan and Heckenberger, 1988; Rutten, 1992]. Two important sources of information are the *Journal of Physical and Chemical Reference Data*, and the data bases maintained by the Chemical and Physical Properties Division of the National Institute of Science and Technology.

Table 1. The convective and molecular fluxes

Entity being transported	Convective flux	Molecular flux
Mass of species α	$\rho_A\mathbf{v}$	$\mathbf{j}_\alpha$
Momentum	$\rho\mathbf{v}\mathbf{v}$	$\boldsymbol{\pi}=p\boldsymbol{\delta}+\boldsymbol{\tau}$
Energy	$\frac{1}{2}\rho v^2\mathbf{v}+\rho\hat{U}\mathbf{v}$	$\mathbf{q}$

In the absence of data, some help can be obtained from experimental correlations based on the principle of corresponding states [BSL, Figs. 1.3-1, 1.3-2, 8.2-1, 16.3-1]. For dilute gases and gas mixtures, responsible estimates can be made using the Chapman-Enskog kinetic theory of gases, along with a realistic intermolecular force expression [Hirschfelder et al., 1964; Waldmann, 1958]. For liquids, the theory is much less well developed, and empiricisms have to be resorted to. Some assistance regarding theory and experiment can be obtained from reviews of the literature [Millat et al., 1996].

2-3. Conservation Laws Leading to the Equations of Change

In this section we give the derivation of the principal partial differential equations needed for formulating transport phenomena problems. These are the four *equations of change* based on the principles of conservation of mass, momentum, energy, and angular momentum. The derivations are given here by applying the conservation laws to an arbitrarily chosen, fixed volume in space (the "control volume") through which any kind of fluid--Newtonian or non-Newtonian--is flowing (see Fig. 5). The equations can also be derived by applying the conservation laws to an arbitrary material element of fluid as it proceeds through space undergoing deformation. In either case one arrives at the equation of continuity, the equation of motion, the equation of energy, and the equation of angular momentum. Here we give the equations in terms of the molecular fluxes, and in Section 2.6 the equations are

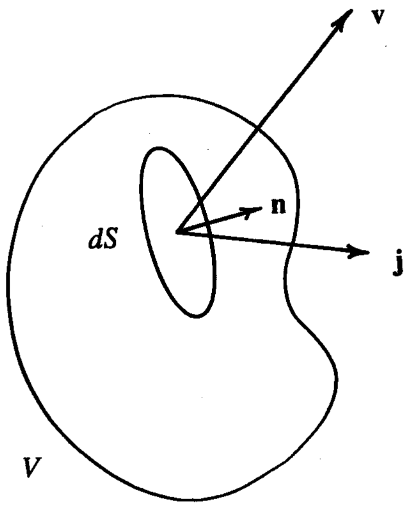


Fig. 5. An arbitrary control volume V, fixed in space, through which a fluid mixture is flowing. At each point on the surface S there is an outwardly directed unit normal vector n. The region inside V is the "minus region", and the region outside V is the "plus region". The mass rate of flow of substance α leaving the volume through the surface element dS by convection is $\rho_\alpha(\mathbf{n}\cdot\mathbf{v})dS$, where v is the mass-average velocity of the fluid. The mass rate of flow of α leaving the volume through dS by diffusion is $(\mathbf{n}\cdot\mathbf{j}_\alpha)dS$. The force exerted by the minus material on the plus material through dS is $[\mathbf{n}\cdot\boldsymbol{\pi}]dS$.

given in terms of the transport properties.

a. The Equations of Continuity

First we apply the law of conservation of mass for species α to the control volume in Fig. 5. This law states that the mass of species α within the volume V increases because of the addition of α across the surface S by convection and by molecular motion (i.e., by diffusion), and because of production of α by chemical reaction. Mathematically this is written as follows:

$$\frac{\mathrm{d}}{\mathrm{dt}}\int_V \rho_\alpha \mathrm{dV} = -\int_S (\mathbf{n}\cdot\rho_\alpha\mathbf{v})\mathrm{dS} - \int_S (\mathbf{n}\cdot\mathbf{j}_\alpha)\mathrm{dS} + \int_V \mathrm{r}_\alpha \mathrm{dV}, \tag{26}$$

in which r_α is the rate of production of mass of species A per unit volume by chemical reactions. On the left side, the time derivative may be taken inside the integral, since the volume V is fixed. The two surface integrals on the right side may be rewritten as volume integrals by using the Gauss divergence theorem (see Eq. (88)). This gives

$$\int_V \frac{\partial}{\partial \mathrm{t}}\rho_\alpha \mathrm{dV} = -\int_V (\nabla\cdot\rho_\alpha\mathbf{v})\mathrm{dV} - \int_V (\nabla\cdot\mathbf{j}_\alpha)\mathrm{dV} + \int_V \mathrm{r}_\alpha \mathrm{dV}. \tag{27}$$

Then, since the volume V was arbitrarily chosen, the integrands may be equated to give

$$\frac{\partial}{\partial \mathrm{t}}\rho_\alpha = -(\nabla\cdot\rho_\alpha\mathbf{v}) - (\nabla\cdot\mathbf{j}_\alpha) + \mathrm{r}_\alpha, \quad \alpha = 1, 2, \ldots \mathrm{N}. \tag{28}$$

This is the *species equation of continuity*. For nonreacting systems, the kinetic theory of gases leads to the same result, but without the last term [see Eq. (12)]; similarly the kinetic theories of liquids and polymers give Eq. (28) [Bearman and Kirkwood, 1958; Curtiss and Bird, 1996b]. When all N equations are added, and when use is made of the relations $\Sigma_\alpha \rho_\alpha = \rho$, $\Sigma_\alpha \mathbf{j}_\alpha = 0$, and $\Sigma_\alpha \mathrm{r}_\alpha = 0$, we obtain

$$\frac{\partial}{\partial \mathrm{t}}\rho = -(\nabla\cdot\rho\mathbf{v}), \tag{29}$$

which is the *equation of continuity* for the fluid mixture. If it can be assumed that the fluid density is constant, Eq. (29) becomes simply $(\nabla\cdot\mathbf{v}) = 0$.

b. The Equation of Motion

We next apply the law of conservation of momentum to the control volume V in Fig. 5. This states that the linear momentum within the volume V increases with time because of the addition of momentum by convection and by molecular processes, and also because of the effect of the external forces acting on the individual species. In mathematical formalism this becomes

$$\frac{\mathrm{d}}{\mathrm{dt}}\int_V \rho\mathbf{v}\mathrm{dV} = -\int_S [\mathbf{n}\cdot\rho\mathbf{v}\mathbf{v}]\mathrm{dS} - \int_S [\mathbf{n}\cdot\boldsymbol{\pi}]\mathrm{dS} + \int_V \Sigma_\alpha \rho_\alpha \mathbf{g}_\alpha \mathrm{dV}, \tag{30}$$

in which $\mathbf{g}_\alpha$ is the force per unit mass acting on species α. Throughout we exclude the possibility of magnetic Lorentz forces. Once again the time-derivative operator can be moved inside the integral, and the two surface integrals on the right can be converted into volume integrals, by using the Gauss divergence theorem as applied to tensors [BSL, Eq. (A. 5-3)]. When the integral signs are removed, we then get

$$\frac{\partial}{\partial \mathrm{t}}\rho\mathbf{v} = -[\nabla\cdot\rho\mathbf{v}\mathbf{v}] - [\nabla\cdot\boldsymbol{\pi}] + \Sigma_\alpha \rho_\alpha \mathbf{g}_\alpha, \tag{31}$$

which is the *equation of motion* for the fluid mixture. If all species have the same force per unit mass acting on them (as would be the case if gravity is the only external force), or, if there is but one chemical species in the fluid, the last term on the right side is just $\rho\mathbf{g}$. The kinetic theory of dilute monatomic gases leads also to Eq. (31), as seen in Eq. (13), and the kinetic theory for monatomic liquids also gives Eq. (31) [Irving and Kirkwood, 1950]. The kinetic theory of polymers leads to an equation that differs from Eq. (31) in the last term; also this theory gives a contribution to $\boldsymbol{\pi}$ associated with the external forces that is not suggested in continuum mechanics derivations [Curtiss and Bird, 1996a, §7 and Appendix A]. When there are conflicts between continuum mechanics results and kinetic theory results, it is clear that the postulates tacitly made in the continuum theory may exclude some effects that the structural theories can explain.

Furthermore, continuum arguments alone are not sufficient for formulating the equations of motion for the individual chemical species; it is possible to develop such equations by means of the molecular theories of monatomic gases [Chapman and Cowling, 1970, Eq. 8.1-7], monatomic liquids [Bearman and Kirkwood, 1958, Eq. 4.20], and polymers [Curtiss and Bird, 1996b, Eq. 21].

c. The Equation of Energy

Next we turn to the application of the principle of conservation of energy to the control volume V. This is, in fact, a statement of the first law of thermodynamics for an open system. It has to be assumed in this derivation that the internal energy per unit mass $\hat{\mathrm{U}}$ is the same function of density, temperature, and concentration as that for equilibrium (From a molecular point of view the internal energy is the sum of the kinetic energies of all the constituent molecules plus the sum of all the intermolecular interaction energies). With these points in mind, we can state the conservation law as follows: the kinetic and internal energy within V increases with time because of the net addition of these two kinds of energy across the surface, because of heat conduction across the surface, because of work done at the surface S by the fluid as it moves across the surface, and because of work done against external forces. In mathematical terms this becomes

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{dt}}\int_V \left(\frac{1}{2}\rho v^2 + \rho\hat{\mathrm{U}}\right)\mathrm{dV} &= -\int_S \left(\mathbf{n}\cdot\left(\frac{1}{2}\rho v^2 + \rho\hat{\mathrm{U}}\right)\mathbf{v}\right)\mathrm{dS}\\ &\quad - \int_S (\mathbf{n}\cdot\mathbf{q})\mathrm{dS} - \int_S (\mathbf{n}\cdot[\boldsymbol{\pi}\cdot\mathbf{v}])\mathrm{dS} + \int_V \Sigma_\alpha((\mathbf{j}_\alpha + \rho_\alpha\mathbf{v})\cdot\mathbf{g}_\alpha)\mathrm{dV}.\end{aligned} \tag{32}$$

After bringing the time-derivative operator inside the integral, converting the surface integrals to volume integrals, and removing the integral signs, we get

$$\begin{aligned}\frac{\partial}{\partial \mathrm{t}}\left(\frac{1}{2}\rho v^2 + \rho\hat{\mathrm{U}}\right) &= -\left(\nabla\cdot\left(\frac{1}{2}\rho v^2 + \rho\hat{\mathrm{U}}\right)\mathbf{v}\right) - (\nabla\cdot\mathbf{q})\\ &\quad -(\nabla\cdot[\boldsymbol{\pi}\cdot\mathbf{v}]) + \Sigma_\alpha((\mathbf{j}_\alpha + \rho_\alpha\mathbf{v})\cdot\mathbf{g}_\alpha),\end{aligned} \tag{33}$$

which is the (*total*) *energy equation*. If there is just one chemical species, or if the external forces acting on all chemical species are identical, the last term on the right side becomes just $(\mathbf{v}\cdot\rho\mathbf{g})$. Eq. (33) is more general than Eq. (14), obtained from the kinetic theory of dilute monatomic gases, since it accounts for the rotational and vibrational energies of the molecules, as well as for the intermolecular potential energies. Eq. (33) is not, however, sufficiently general to account for some additional effects that arise in the energy equation for polymeric liquid mixtures [see Curtiss and Bird, 1996a, Eqs. (8.1) and (8.15)].

d. The Equation of Angular Momentum

Finally we apply the law of conservation of momentum to the control volume V of Fig. 5. This states that the total angular momentum (including the flow angular momentum and the internal angular momentum) within V increases with time because of the addition of angular momentum by convection and by molecular processes, and also becaue of the action of external torques and the torques associated with the external forces. When this is captured in mathematical form we have

$$\begin{aligned}\frac{d}{dt}\int_V(\rho[\mathbf{r}\times\mathbf{v}]+\rho\hat{\mathbf{L}})dV &= -\int_S(\mathbf{n}\cdot\mathbf{v})(\rho[\mathbf{r}\times\mathbf{v}]+\rho\hat{\mathbf{L}})dS\\ &-\int_S[\mathbf{n}\cdot\boldsymbol{\lambda}]dS-\int_S[\mathbf{r}\times[\mathbf{n}\times\boldsymbol{\pi}]]dS+\int_V[\mathbf{r}\times\Sigma_\alpha\rho_\alpha\mathbf{g}_\alpha]dV\\ &+\int_V\Sigma_\alpha\rho_\alpha\mathbf{t}_\alpha dV. \end{aligned} \tag{34}$$

Here $\hat{\mathbf{L}}$ is the internal angular momentum per unit mass, $\boldsymbol{\lambda}$ is the molecular flux of angular momentum, and $\mathbf{t}_\alpha$ represents the external torque per unit mass acting on species α. When this integral conservation equation is treated in a manner similar to that for the other conservation statements, we get the *equation of change for angular momentum* in the form [Dahler and Scriven, 1961]

$$\begin{aligned}\frac{\partial}{\partial t}(\rho[\mathbf{r}\times\mathbf{v}]+\rho\hat{\mathbf{L}}) &= -[\nabla\cdot(\rho\mathbf{v}[\mathbf{r}\times\mathbf{v}]+\rho\mathbf{v}\hat{\mathbf{L}})]-[\nabla\cdot\boldsymbol{\lambda}]\\ &-[\nabla\cdot\{\mathbf{r}\times\boldsymbol{\pi}^\dagger\}^\dagger]+[\mathbf{r}\times\Sigma_\alpha\rho_\alpha\mathbf{g}_\alpha]+\Sigma_\alpha\rho_\alpha\mathbf{t}_\alpha. \end{aligned} \tag{35}$$

This equation has seldom been used, because of the lack of information about the molecular angular momentum flux and the internal angular momentum flux per unit mass.

e. The Substantial Derivative Forms of the Equations of Change

The equations of change can be written in two ways: the ∂/∂t-form (in which the changes at one point in 3-dimensional space are described, as above) and the D/Dt-form (in which the changes following one material element of fluid are described). We now discuss the relation between these two forms of the equations.

To begin with, there are two ways to describe fluid motion:

(a) In the *Eulerian description*, we specify the *fluid velocity* at all locations **r** in space for all times t. That is we describe the motion by giving **v**(**r**, t).

(b) In the *Lagrangian description*, we specify the locations of all *fluid particles* for all times t. If a fluid particle is located at position **r**' in space at some past time t', and if that same particle is located at **r** at the current time t, then the motion of a fluid particle is given by the function **r**=**r**(**r**', t', t); that is the location of the fluid particle **r**', t' will be at **r** at time t. Note that **r**', t' is used as a "particle label". [We use the term "fluid particle" for a tiny "lump" of the fluid within the continuum and not to an individual molecule.]

The *velocity of a fluid particle* at time t is given by

$$\mathbf{v}_P(\mathbf{r}', t', t)=\frac{\partial}{\partial t}\mathbf{r}(\mathbf{r}', t', t). \tag{36}$$

That is, we differentiate the particle position **r** with respect to the time t for the given particle **r**', t' (that is, we take $\partial/\partial t$ holding **r**', t' constant). The fluid velocity at **r** at time t is exactly the same as the fluid particle velocity at the same point, so that

$$\mathbf{v}_P(\mathbf{r}', t', t)=\mathbf{v}(\mathbf{r}, t). \tag{37}$$

The fact that there are two ways of describing fluid motion leads to two kinds of time derivatives: we can describe how a quantity is changing at a fixed position in space (the *partial derivative* $\partial/\partial t$, in which **r** is held constant), or we can describe how some quantity changes at a fixed particle as it moves through space (the *substantial derivative* D/Dt, in which the particle label **r**', t' is held constant).

For example, for a scalar quantity, such as temperature, we can define two quantities: T(**r**, t) the temperature of the fluid at position **r** and time t, or T_P(**r**', t', t), the temperature of the fluid at the fluid particle **r**', t' at time t. Since these quantities are numerically the same, we can write

$$T_P(\mathbf{r}', t', t)=T(\mathbf{r}, t). \tag{38}$$

The time rate of change of the fluid temperature following some fluid particle, can be obtained by differentiating this equation with respect to t holding the particle label constant; to do this we use the chain rule of partial differentiation to get

$$\begin{aligned}\left(\frac{\partial}{\partial t}T_P\right)_{r',t'} &= \left(\frac{\partial T}{\partial t}\right)_r+\left(\frac{\partial x}{\partial t}\right)_{r',t'}\left(\frac{\partial T}{\partial x}\right)_{y,z,t}+\left(\frac{\partial y}{\partial t}\right)_{r',t'}\left(\frac{\partial T}{\partial y}\right)_{z,x,t}\\ &+\left(\frac{\partial z}{\partial t}\right)_{r',t'}\left(\frac{\partial T}{\partial z}\right)_{x,y,t} \end{aligned} \tag{39}$$

Since $(\partial x/\partial t)_{r',t'}$ is the x-component of the fluid particle velocity $\mathbf{v}_P$(**r**', t', t) which in turn is the x-component of the fluid velocity **v**(**r**, t), we may then write

$$\begin{aligned}\left(\frac{\partial}{\partial t}T_P\right)_{r',t'} &= \left(\frac{\partial T}{\partial t}\right)_r+v_x\left(\frac{\partial T}{\partial x}\right)_{y,z,t}+v_y\left(\frac{\partial T}{\partial y}\right)_{z,x,t}\\ &+v_z\left(\frac{\partial T}{\partial z}\right)_{x,y,t} \end{aligned} \tag{40}$$

Then if we choose to designate $(\partial T_P/\partial t)_{r',t'}$ by the less cumbersome symbol DT/Dt, we have

$$\frac{DT}{Dt}=\frac{\partial T}{\partial t}+(\mathbf{v}\cdot\nabla T). \tag{41}$$

The operator D/Dt is called the *substantial derivative* (or *material derivative*) since it describes how some quantity changes with time as one moves along with the substance (or material).

Similarly, applying the chain rule of partial differentiation to Eq. (36) and following a similar procedure, we get for the substantial derivative of the velocity

$$\frac{D\mathbf{v}}{Dt}=\frac{\partial\mathbf{v}}{\partial t}+[\mathbf{v}\cdot\nabla\mathbf{v}]. \tag{42}$$

That is, the symbol Dv/Dt describes the change of the velocity of the fluid particle with time--that is, the fluid particle acceleration. Note that the operation $[\mathbf{v}\cdot\nabla\mathbf{v}]$ may also be written as $(\mathbf{v}\cdot\nabla)\mathbf{v}$; for some purposes it is useful to write it as $\frac{1}{2}\nabla(\mathbf{v}\cdot\mathbf{v})$-$[\mathbf{v}\times[\nabla\times\mathbf{v}]]$.

To interconvert equations between the D/Dt notation and the ∂/∂t notation, the relations

$$\rho\frac{\mathrm{D}X}{\mathrm{D}t}=\frac{\partial}{\partial t}\rho X+(\rho\mathbf{v}\cdot\nabla X),\text{ and }\rho\frac{\mathrm{D}\mathbf{X}}{\mathrm{D}t}=\frac{\partial}{\partial t}\rho\mathbf{X}+[\rho\mathbf{v}\cdot\nabla\mathbf{X}],\quad(43)$$

are used for scalar (X) and vector (**X**) quantities respectively. The derivation of these relations requires the use of the equation of continuity.

We now summarize the equations of continuity, motion, energy, and angular momentum written in terms of the D/Dt notation. It should be emphasized that no assumptions are introduced in going from the ∂/∂t forms of the conservation equations to the D/Dt forms.

$$\text{Mass: }\frac{\mathrm{D}\rho}{\mathrm{D}t}=-\rho(\nabla\cdot\mathbf{v}),\quad(44)$$

$$\text{Mass of Species }\alpha:\ \rho\frac{\mathrm{D}\omega_\alpha}{\mathrm{D}t}=-(\nabla\cdot\mathbf{j}_\alpha)+r_\alpha,\quad(45)$$

$$\text{Momentum: }\rho\frac{\mathrm{D}\mathbf{v}}{\mathrm{D}t}=-[\nabla\cdot\boldsymbol{\pi}]+\Sigma_\alpha\rho_\alpha\mathbf{g}_\alpha,\quad(46)$$

$$\text{Energy: }\rho\frac{\mathrm{D}}{\mathrm{D}t}\left(\frac{1}{2}v^2+\hat{U}\right)=-(\nabla\cdot\mathbf{q})-(\nabla\cdot[\boldsymbol{\pi}\cdot\mathbf{v}])$$
$$+\Sigma_\alpha((\mathbf{j}_\alpha+\rho_\alpha\mathbf{v})\cdot\mathbf{g}_\alpha).\quad(47)$$

$$\text{Angular Momentum: }\rho\frac{\mathrm{D}}{\mathrm{D}t}([\mathbf{r}\times\mathbf{v}]+\hat{\mathbf{L}})=-[\nabla\cdot\boldsymbol{\lambda}]$$
$$-[\nabla\cdot\{\mathbf{r}\times\boldsymbol{\pi}^\dagger\}^\dagger]+[\mathbf{r}\times\Sigma_\alpha\rho_\alpha\mathbf{g}_\alpha]+\Sigma_\alpha\rho_\alpha\mathbf{t}_\alpha\quad(48)$$

These equations, together with the expressions for the fluxes and the thermal equation of state $[p=p(\hat{V}, T, \omega_1, \omega_2, \omega_3, \ldots)]$ and the caloric equation of state $[\hat{U}=\hat{U}(\hat{V}, T, \omega_1, \omega_2, \omega_3, \ldots)]$ form a complete set of equations which can be solved with the appropriate boundary conditions

2-4. Other Equations of Change

The five equations of change derived in the foregoing section, Eqs. (44) to (48), are based on the principles of conservation of species mass, total mass, momentum, energy, and angular momentum. In this section we present several additional equations of change that can be obtained from the conservation equations.

a. The Equation of Change for Mechanical Energy

By forming the dot product of the local fluid velocity vector v with the equation of motion, we obtain the following result:

$$\rho\frac{\mathrm{D}}{\mathrm{D}t}\left(\frac{1}{2}v^2\right)=-(\nabla\cdot[\boldsymbol{\pi}\cdot\mathbf{v}])+(\boldsymbol{\pi}:\nabla\mathbf{v})+\sum_\alpha\rho_\alpha(\mathbf{v}\cdot\mathbf{g}_\alpha),\quad(49)$$

which is the *mechanical energy equation.* For fluids with a single chemical species, or if the only external forces result from the gravitational field, the last term becomes $\rho(\mathbf{v}\cdot\mathbf{g})$. If the gravity force acts in the negative z direction, and if the equation is further simplified by assuming steady state and an inviscid fluid, then the equation can be put into the form

$$\rho\nabla\frac{1}{2}v^2-\rho[\mathbf{v}\times[\nabla\times\mathbf{v}]]=-\nabla p-\rho g\nabla z,\quad(50)$$

Then we form the dot product of this equation with the unit vector in the flow direction, $\mathbf{s}=\mathbf{v}/|\mathbf{v}|$, and write $(\mathbf{s}\cdot\nabla)=d/ds$ where s is the distance along a streamline. Then integration along the streamline from point "1" to point "2" gives the *Bernoulli equation* for the steady-state flow of a hypothetical inviscid fluid

$$\frac{1}{2}(v_2^2-v_1^2)+\int_{p_1}^{p_2}\frac{1}{\rho}dp+g(z_2-z_1)=0.\quad(51)$$

This equation interrelates the pressures, the velocities, and elevations at points "1" and "2" along a streamline. This same equation can be found by integrating the energy equation for isentropic flow along a streamline [Bird and Graham, 1997].

b. The Equation of Change for Internal Energy

When the mechanical energy equation of Eq. (49) is subtracted from the total energy equation, we obtain

$$\rho\frac{\mathrm{D}}{\mathrm{D}t}\hat{U}=-(\nabla\cdot\mathbf{q})-(\boldsymbol{\pi}:\nabla\mathbf{v})+\sum_\alpha(\mathbf{j}_\alpha\cdot\mathbf{g}_\alpha),\quad(52)$$

which is the *internal energy equation*. For fluids containing one chemical species only, the last term is zero. Note that the quantity $(\boldsymbol{\pi}:\nabla\mathbf{v})$ appears in Eqs. (49) and (52) with opposite signs, indicating that this quantity describes how energy is interconverted between the mechanical and internal forms. Note further that, if the sole external force is that of gravity, then the last term in Eq. (52) is zero.

c. The Equation of Change for Temperature

From Eq. (52) we may obtain an equation of change for enthalpy by replacing $\hat{U}$ by $\hat{H}$-(p/ρ). Then, it is assumed that $\hat{H}$ can be expressed as a function of p, T, and composition, and furthermore that the standard formulas from equilibrium thermodynamics can be used [see BSL, §10.1]; with these assumptions the enthalpy equation can be transformed into the following equation for the temperature, which is generally more useful:

$$\rho\hat{C}_p\frac{\mathrm{D}T}{\mathrm{D}t}=-(\nabla\cdot\mathbf{q})-(\boldsymbol{\tau}:\nabla\mathbf{v})+p(\nabla\cdot\mathbf{v})+\sum_\alpha(\mathbf{j}_\alpha\cdot\mathbf{g}_\alpha)$$
$$-\left(\frac{\partial\ln\rho}{\partial\ln T}\right)_{p,\omega_\alpha}\frac{\mathrm{D}p}{\mathrm{D}t}+\sum_\alpha(\bar{H}_\alpha/M_\alpha)[(\nabla\cdot\mathbf{j}_\alpha)-r_\alpha].\quad(53)$$

in which the $\bar{H}_\alpha$ are the partial molar enthalpies. For pure fluids the terms involving diffusion and chemical reaction are zero. The energy equation can be put into many other forms [BSL, Tables 10.4-1 and 18.3-1].

For polymeric liquids it is not possible to make the step from Eq. (52) to Eq. (53), because the enthalpy is not simply a function of temperature, pressure, and composition [for a short discussion, see Christensen, 1982, Chapter 3 for a continuum-mechanics treatment for linear viscoelastic fluids, and Curtiss and Bird, 1996a, Appendix C, for a lowest-order molecular treatment for nonlinear viscoelastic fluids].

d. The Equation of Change for Bulk Angular Momentum

If the cross product is formed between the position vector **r** and the equation of motion, the following *equation of bulk angular momentum* results:

$$\rho\frac{\mathrm{D}}{\mathrm{Dt}}[\mathbf{r}\times\mathbf{v}]=-[\nabla\cdot\{\mathbf{r}\times\boldsymbol{\pi}^{\dagger}\}^{\dagger}]+\rho[\mathbf{r}\times\sum_{\alpha}\rho_{\alpha}\mathbf{g}_{\alpha}]+[\boldsymbol{\varepsilon}:\boldsymbol{\pi}^{\dagger}]. \qquad (54)$$

Here $\boldsymbol{\varepsilon}$ is a third-order tensor with components $\varepsilon_{ijk}=\frac{1}{2}(i-j)(j-k)(k-i)$. Eq. (54) was obtained from the equation of motion without assuming the symmetry of $\boldsymbol{\pi}$. If Eq. (54) is subtracted from the D/Dt form of the total angular momentum equation in Eq. (35), one gets the *equation of change for internal angular momentum*. In this equation there appears the term $-[\boldsymbol{\varepsilon}:\boldsymbol{\pi}^{\dagger}]$, that is, the last term in Eq. (54), but with the opposite sign. Thus this term couples the internal angular momentum equation to the bulk angular momentum equation and describes the way in which the two forms of angular momentum are interconverted. For Newtonian fluids, for which $\boldsymbol{\pi}$ is known to be symmetric, the transpose sign may be removed from the symbol $\boldsymbol{\pi}$, and, in addition, the term $[\boldsymbol{\varepsilon}:\boldsymbol{\pi}^{\dagger}]$ is zero. Thus the assumption of a symmetric stress tensor implies that there is no interconversion between internal and bulk angular momentum associated with the flow, and Eq. (54) suffices for describing the angular momentum in a flowing system.

The assumption of the symmetry of $\boldsymbol{\pi}$ has been normally made in discussion of fluid dynamics. The kinetic theories for monatomic gases [Chapman and Cowling, 1970], monatomic liquids [Irving and Kirkwood, 1950], and polymers [Curtiss and Bird, 1996a] indicate that the assumption of symmetric $\boldsymbol{\pi}$ is valid [for futher comments and literature references regarding the symmetry of the stress tensor, see Dahler and Scriven, 1961; Dahler and Scriven, 1963; Condiff and Dahler, 1964; Dahler, 1965; Kuiken, 1995; Serrin, 1959, §7].

e. The Equation of Change for Entropy

For the sake of simplicity, in this subsection, only binary mixtures are considered. To obtain the entropy equation we need the following differential relation from equilibrium thermodynamics:

$$\mathrm{d}\hat{\mathrm{U}}=\mathrm{T}\mathrm{d}\hat{\mathrm{S}}+(\mathrm{p}/\rho^2)\mathrm{d}\rho+[(\overline{\mathrm{G}}_A/\mathrm{M}_A)-(\overline{\mathrm{G}}_B/\mathrm{M}_B)\mathrm{d}\omega_A. \qquad (55)$$

Here $\overline{\mathrm{G}}_A$ is the partial molar Gibbs free energy. This is then substituted into Eq. (50). Then $\mathrm{D}\omega_A/\mathrm{Dt}$ and $\mathrm{D}\rho/\mathrm{Dt}$ are eliminated by using the species equation of continuity, Eq. (45) and the total equation of continuity (Eq. (44)). In this way, one obtains, after some rearrangement, the following *entropy equation*:

$$\rho\frac{\mathrm{D}\hat{\mathrm{S}}}{\mathrm{Dt}}=-(\nabla\cdot\mathbf{s})+\mathrm{g}_s, \qquad (56)$$

in which $\mathbf{s}$ is the *entropy flux* and g_s is the *entropy production*, given by

$$\mathbf{s}=\frac{1}{\mathrm{T}}(\mathbf{q}-\mu_{AB}\mathbf{j}_A)=\frac{1}{\mathrm{T}}(\mathbf{q}-\sum_{\alpha}(\overline{\mathrm{H}}_{\alpha}/\mathrm{M}_{\alpha})\mathbf{j}_{\alpha})+(\sum_{\alpha}(\overline{\mathrm{S}}_{\alpha}/\mathrm{M}_{\alpha})\mathbf{j}_{\alpha}), \qquad (57)$$

$$\mathrm{g}_s=-\left((\mathbf{q}-\mu_{AB}\mathbf{j}_A)\cdot\frac{1}{\mathrm{T}^2}\nabla\mathrm{T}\right)-\left(\mathbf{j}_A\cdot\frac{1}{\mathrm{T}}(\nabla\mu_{AB}+(\mathbf{g}_B-\mathbf{g}_A))\right)$$
$$-\mathrm{r}_A\left(\frac{1}{\mathrm{T}}\mu_{AB}\right)-\left(\boldsymbol{\tau}:\frac{1}{\mathrm{T}}\nabla\mathbf{v}\right). \qquad (58)$$

Here $\mu_{AB}=(\overline{\mathrm{G}}_A/\mathrm{M}_A)-(\overline{\mathrm{G}}_B/\mathrm{M}_B)$, and the summations in Eq. (57) just extend over A and B. The entropy generation has been written in Eq. (57) as a sum of products of "fluxes" and "forces". This provides the starting point for the discussion of the nonequilibrium thermodynamics of the transport phenomena in §2-5.

2-5. The Molecular Fluxes from Nonequilibrium Thermodynamics

It was pointed out that the expressions given in Section 2-2 for the fluxes are incomplete. Here we show how nonequilibrium thermodynamics can provide additional insight into the formulas for the molecular fluxes.

In extending thermodynamics from equilibrium to nonequilibrium systems it is necessary to add the following:

a. It is assumed that locally, the standard relations among thermodynamic quantities for systems in equilibrium are also valid in nonequilibrium situations. We already used this idea in obtaining the equation of change for temperature from the internal energy equation.

b. It is assumed that the relations between the fluxes and the driving forces can are linear, and that fluxes can result from all forces present. That is, $(\text{flux})_j=\Sigma_k\alpha_{jk}\,(\text{force})_k$, in which the α_{jk} are coefficients independent of the forces and fluxes.

c. In (b) there is coupling between fluxes and forces only when the tensorial orders of the fluxes and forces are the same or differ by 2 (*Curie's law*).

d. The matrix of coefficients α_{jk} is symmetric (in the absence of magnetic fields); the relations $\alpha_{jk}=\alpha_{kj}$ are called the *Onsager reciprocal relations*.

With these statements in hand we can now make use of the entropy production expression in (Eq. (58)).

If we now make use of statements (b) and (c) above, and if we use the abbreviation $\nabla\mu'_{AB}=\nabla\mu_{AB}+(\mathbf{g}_B-\mathbf{g}_A)$, the expressions for the mass and energy fluxes are:

$$\mathbf{j}_A=-\alpha_{11}\frac{1}{\mathrm{T}}\nabla\mu'_{AB}-\alpha_{12}\frac{1}{\mathrm{T}^2}\nabla\mathrm{T}, \qquad (59)$$

$$\mathbf{q}-\mu\mathbf{j}_A=-\alpha_{12}\frac{1}{\mathrm{T}}\nabla\mu'_{AB}-\alpha_{22}\frac{1}{\mathrm{T}^2}\nabla\mathrm{T}. \qquad (60)$$

We solve the first equation for $\nabla\mu'_{AB}$ and substitute it into the second to get

$$\mathbf{q}=\left(\mu+\frac{\alpha_{12}}{\alpha_{11}}\right)\mathbf{j}_A-\left(\alpha_{22}-\frac{\alpha_{12}^2}{\alpha_{11}}\right)\frac{1}{\mathrm{T}^2}\nabla\mathrm{T}. \qquad (61)$$

The coefficient of $\nabla\mathrm{T}$ in this equation is defined to be the *thermal conductivity* of the mixture (and *not* the coefficient of $\nabla\mathrm{T}$ in the preceding equation).

Next we develop the expression for the mass flux. Since μ_{AB} is not a convenient variable, we consider it to be a function of ω_A, T, and p, so that

$$\nabla\mu_{AB}=\left(\frac{\partial\mu_{AB}}{\partial\omega_A}\right)_{p,T}\nabla\omega_A+\left(\frac{\partial\mu_{AB}}{\partial\mathrm{T}}\right)_{p,\omega_A}\nabla\mathrm{T}+\left(\frac{\partial\mu_{AB}}{\partial\mathrm{p}}\right)_{T,\omega_A}\nabla\mathrm{p}. \qquad (62)$$

Then Eq. (59) assumes the form

$$\mathbf{j}_A=-\rho\mathfrak{D}_{AB}[\nabla\omega_A+\mathrm{k}_T\nabla\mathrm{T}+\mathrm{k}_p\nabla\mathrm{p}+\mathrm{k}_F(\mathbf{g}_B-\mathbf{g}_A)], \qquad (63)$$

in which the coefficients $\mathfrak{D}_{AB}$, k_T, k_p, and k_F are given by

$$\rho\mathfrak{D}_{AB} = \frac{\alpha_{11}}{\mathrm{T}}\left(\frac{\partial \mu_{AB}}{\partial \omega_A}\right)_{p,T} = \frac{\alpha_{11}}{\mathrm{T}}\left(\frac{\mathrm{MRT}(\partial \ln a_A/\partial \ln x_A)_{p,T}}{\mathrm{M}_A \mathrm{M}_B\, \omega_A\, \omega_B}\right), \tag{64}$$

$$\rho\mathfrak{D}_{AB}\frac{\mathrm{k}_T}{\mathrm{T}} = \frac{\alpha_{11}}{\mathrm{T}}\left(\frac{\partial \mu_{AB}}{\partial \mathrm{T}}\right)_{p,\omega_A} + \frac{\alpha_{12}}{\mathrm{T}^2}, \tag{65}$$

$$\rho\mathfrak{D}_{AB}\frac{\mathrm{k}_p}{\mathrm{p}} = \frac{\alpha_{11}}{\mathrm{T}}\left(\frac{\partial \mu_{AB}}{\partial \mathrm{p}}\right)_{T,\omega_A} = \frac{\alpha_{11}}{\mathrm{T}}\left(\frac{\partial \hat{\mathrm{V}}}{\partial \omega_A}\right)_{T,p}, \tag{66}$$

$$\rho\mathfrak{D}_{AB}\mathrm{k}_F = \frac{\alpha_{11}}{\mathrm{T}}. \tag{67}$$

Here k_T is the *coefficient of thermal diffusion*. In going from Eq. (59) to Eq. (63), α_{11} and α_{12} have been replaced by $\mathfrak{D}_{AB}$ and k_T (the coefficients k_p and k_F are just expressed in terms of $\mathfrak{D}_{AB}$ and quantities derivable from the equation of state of the fluid). Eq. (63) shows that a mass flux can result from concentration gradients (ordinary diffusion), from temperature gradients (thermal diffusion or the *Soret effect*), from pressure gradients (pressure diffusion), and from external forces (forced diffusion) [cf. BSL, Eq. (18.4-15), and also Eqs. (18.4-8) to (18.4-11), where no derivations were given].

Next we return to the expression for the heat flux **q** given in Eq. (61). When we make use of the definition of thermal conductivity and an expression for the ratio α_{12}/α_{11} that can be obtained from Eqs. (64) and (65), the energy flux becomes

$$\begin{aligned}\mathbf{q} &= \left(\mu_{AB} - \mathrm{T}\left(\frac{\partial \mu_{AB}}{\partial \mathrm{T}}\right)_{p,\omega_A} + \mathrm{k}_T\left(\frac{\partial \mu_{AB}}{\partial \omega_A}\right)_{T,p}\right)\mathbf{j}_A - \mathrm{k}\nabla\mathrm{T} \\ &= -\mathrm{k}\nabla\mathrm{T} + \left(\frac{\bar{\mathrm{H}}_A}{\mathrm{M}_A} - \frac{\bar{\mathrm{H}}_B}{\mathrm{M}_B}\right)\mathbf{j}_A + \mathrm{k}_T\left(\frac{\partial \mu_{AB}}{\partial \omega_A}\right)_{T,p}\mathbf{j}_A.\end{aligned} \tag{68}$$

This shows that the heat flux contains one term associated with the temperature gradient (heat conduction), a term resulting from diffusion, and a third (very small) term which is referred to as the *Dufour effect* or the *diffusion-thermo effect*. This term does not appear in Eq. (24) [see also BSL, Eqs. (18.4-2) and (18.4-3), where no derivation was given; for in-depth discussions of the nonequilibrium thermodynamics as applied to transport phenomena, see de Groot and Mazur, 1962; Landau and Lifshitz, 1987; Hirschfelder et al., 1964; for extensions to nonlinear transport phenomena see Beris and Edwards, 1994; Grmela and Öttinger, 1997; Öttinger and Grmela, 1997; Öttinger, 1998].

2-6. The Equations of Change in Terms of the Transport Properties

When the conservation equations in Eqs. (44) to (48) are combined with the flux expressions in Eqs. (22) to (24), we get the equations that are to be solved for Newtonian fluids for the pressure, composition, velocity, and temperature. These are the starting equations that are used when one is doing a complete numerical solution of a problem, with the temperature, concentration, and pressure dependence of all physical properties being taken into account. To get analytical solutions to idealized problems, the equations are often simplified by assuming constant physical properties and possibly discarding unimportant terms (for example, the dissipation terms in the energy equation, when the viscosity and the velocity gradients are appropriately small). In this section we present some of the standard approximate equations that have been widely used in textbooks and research publications.

a. The Equations for Diffusion

Substitution of the expression for the mass flux in Eq. (22) into the species continuity equation gives for a binary mixture:

$$\rho\frac{\mathrm{D}\omega_A}{\mathrm{Dt}} = (\nabla\cdot\rho\mathfrak{D}_{AB}\nabla\omega_A) + \mathrm{r}_A. \tag{69}$$

However, if it is appropriate to assume that the density and diffusivity are constant, then Eq. (69) becomes the *diffusion equation*,

$$\frac{\mathrm{D}\rho_A}{\mathrm{Dt}} = \mathfrak{D}_{AB}\nabla^2\rho_A + \mathrm{r}_A. \tag{70}$$

To solve this equation, many analytical methods are known and many solutions tabulated [Crank, 1956; Aris, 1975]. Chemical reactions taking place in the body of the fluid and are described by the term r_A are referred to as *homogeneous* chemical reactions; reactions occurring at a solid surface (such as a catalytic surface) are called a *heterogeneous* chemical reactions and are described by means of the boundary conditions.

b. The Equation of Motion

When the Newtonian expression for the stress tensor is substituted into the equation of motion, and when it is assumed that the fluid has constant density and viscosity, the following equation is obtained for a pure fluid:

$$\rho\frac{\mathrm{D}\mathbf{v}}{\mathrm{Dt}} = -\nabla\mathrm{p} + \mu\nabla^2\mathbf{v} + \rho\mathbf{g}, \quad \text{or} \quad \rho\frac{\mathrm{D}\mathbf{v}}{\mathrm{Dt}} = -\nabla\mathcal{P} + \mu\nabla^2\mathbf{v}, \tag{71}$$

in which $\mathcal{P} = \mathrm{p} + \rho\hat{\Phi}$ is referred to as the *modified pressure.* Many solutions to the Navier-Stokes equations have been worked out [Villat and Kravtchenko, 1943; Dryden et al., 1956; Berker, 1963]. For flows with two nonvanishing velocity components, reformulation of the problem in terms of the stream function is often helpful [BSL, §4.2; Goldstein, 1938; Bird et al., 1987a, Table 1.4-1]. For some laminar flow problems analytical solutions can be obtained by asymptotic methods or by using scaling arguments [Leal, 1992].

If, in addition, it assumed that the viscous forces are negligible, then Eq. (71) becomes *Euler's equation of motion* for inviscid fluids.

$$\rho\frac{\mathrm{D}\mathbf{v}}{\mathrm{Dt}} = -\nabla\mathcal{P} + \rho\mathbf{g}, \tag{72}$$

Many analytical solutions are known for this equation [Lamb, 1932; Milne-Thompson, 1955; Frisch, 1995].

For *creeping flow* (sometimes called *Stokes flow*) one can omit the left side of Eq. (71) and obtain

$$0 = -\nabla\mathcal{P} + \mu\nabla^2\mathbf{v}, \tag{73}$$

which is the basis for *low Reynolds number hydrodynamics* [Happel and Brenner, 1983; Kim and Karrila, 1991]. This equation, with specified boundary conditions, may be reformulated as a problem in the calculus of variations; this is referred to as the *Helmholtz-Korteweg variational principle* [Lamb, 1932; Bird et al., §4.3, 1987a; Carey and Oden, 1986].

By taking the curl of the Navier-Stokes equation in Eq. (71), the *equation for vorticity* may be obtained in either of two forms

$$\frac{D\mathbf{w}}{Dt} = [\mathbf{w} \cdot \nabla \mathbf{v}] + \nu \nabla^2 \mathbf{w}, \text{ or } \frac{D\mathbf{w}}{Dt} = [\boldsymbol{\varepsilon} : \{\nabla \mathbf{v} \cdot \nabla \mathbf{v}\}] + \nu \nabla^2 \mathbf{w}, \qquad (74)$$

in which $\mathbf{w}=[\nabla \times \mathbf{v}]$ is the *vorticity vector* and ν is the kinematic viscosity. Note that one-half the vorticity vector is just the *local angular velocity* of the fluid. In two-dimensional flows $[\mathbf{w} \cdot \nabla \mathbf{v}]$ vanishes, and the vorticity $\mathbf{w}$ satisfies a diffusion equation [Batchelor, 1967; Serrin, 1959, §40]. The vorticity vector is used in defining the corotating coordinate frame that leads to the Jaumann derivative used in rheology [Bird et al., 1977, Chapter 7]. There are, however, other kinematic quantities that can be used to define rotating coordinate systems for use in constructing rheological constitutive equations [see Wedgewood and Geurts, 1995].

c. The Equation of Energy

For a pure fluid, insertion of Newton's law and Fourier's law (Eqs. (23) and (24)) into the energy equation, Eq. (26), gives

$$\rho \hat{C}_p \frac{DT}{Dt} = (\nabla \cdot k \nabla T) - \left(\frac{\partial \ln \rho}{\partial \ln T} \right)_p \frac{Dp}{Dt} + \Phi, \qquad (75)$$

in which Φ is the *dissipation function*, defined by

$$\Phi = \frac{1}{2}\mu \left(\left[\nabla \mathbf{v} + (\nabla \mathbf{v})^{\dagger} - \frac{2}{3}(\nabla \cdot \mathbf{v})\boldsymbol{\delta} \right] : \right.$$

$$\left. [\nabla \mathbf{v} + (\nabla \mathbf{v})^{\dagger} - \frac{2}{3}(\nabla \cdot \mathbf{v})\boldsymbol{\delta}] \right) + \kappa(\nabla \cdot \mathbf{v})^2. \qquad (76)$$

Since, for Newtonian fluids, the dissipation function is a sum of squares, it is a positive quantity. It describes the irreversible conversion of mechanical energy into heat. The last term in the entropy equation (Eq. (58)) is the dissipation function divided by the temperature.

If the thermal conductivity and fluid density are both constant, Eq. (75) simplifies to

$$\rho \hat{C}_p \frac{DT}{Dt} = k \nabla^2 T + \Phi, \qquad (77)$$

and the terms containing $(\nabla \cdot \mathbf{v})$ in the dissipation function vanish. If the viscous dissipation is sufficiently small that it can be neglected, Eq. (77) is identical in form to Equation (70) if no chemical reactions are occurring. The similarity of the two equations is the basis for discussions of analogies between heat and mass transport problems. Many solutions of the heat conduction equation are available [Carslaw and Jaeger, 1959; Leal, 1992].

d. Boundary Conditions

All of the differential equations given in this section must be solved with boundary and initial conditions. Although the differential equations are generally agreed upon, the choice of boundary conditions can sometimes be controversial. The reason for this is that sometimes the physical or chemical situations at the boundaries of the system may not be well understood.

In solving the Navier-Stokes equation it is customary to assume that the fluid "clings" to the bounding surfaces, so that fluid velocity $\mathbf{v}$ is equal to the velocity of the surface. This well-known "no-slip" boundary condition has been challenged [Richardson, 1973]; the "no-slip" condition on smooth walls turns out to be equivalent to a "complete slip" boundary condition at a corrugated surface! For some problems, it may be possible to specify the shearing force at the surface (the viscous normal stresses are zero for Newtonian fluids for any kind of flow, when the assumption of incompressibility is made). At a plane interface between two immiscible liquids, the usual interfacial conditions are that the fluid velocity and the normal component of the momentum flux are continuous. At the interface between a liquid and a gas, it is often assumed that there is no momentum transfer between the liquid and the gas. For the Euler equation of motion for the (fictitious) inviscid fluid the component of $\mathbf{v}$ normal to a fixed surface must be zero, but the tangential component is free to take on any value.

For problems in nonisothermal flow, at the bounding surfaces one can specify the temperature or the heat flux. At the interface between a solid and a fluid, in solving the heat conduction equation in the solid region, one may assume that the heat loss from the solid to the fluid is proportional to the difference between the solid surface temperature and the temperature in the bulk of the fluid, and the proportionality coefficient is called the "heat transfer coefficient". This is sometimes referred to as *Newton's law of cooling*.

For problems involving mixtures, one can specify the concentration or the mass flux at the bounding surfaces. Also, one can specify the rate at which a material disappears at a catalytic surface when there is a heterogeneous chemical reaction. In addition, the diffusional analog of Newton's law of cooling can be used, with the coefficient of proportionality being referred to as the "mass-transfer coefficient". In evaporating systems, it is customary to assume that the concentration of the evaporated liquid in the gas phase is related to the equilibrium vapor pressure of the liquid; this "equilibrium at the interface" assumption can be questioned, particularly when rapid evaporation of a highly volatile liquid is involved.

For gases at low density, in the Knudsen region, it is not possible to use the boundary conditions that the velocity, temperature, and concentration in the fluid are the same as the corresponding quantities of the wall. Instead, one has to introduce the notion of viscous slip, temperature slip, and diffusion slip at the surfaces.

2-7. Polymeric Liquids

Polymeric liquids pose a special problem for the chemical engineer, since they are *non-Newtonian liquids*; that is, they are not described by Eq. (23). From the viewpoint of engineering calculations, probably the most important feature of these fluids is fact that in a steady shear flow the viscosity is found to depend very strongly on the velocity gradient. This can be described very easily by introducing empirical expressions in which the viscosity depends on the velocity gradient (the *generalized Newtonian models*). The "power-law model", the "Eyring model", the "Carreau model", and many others have been widely used and are reasonably successful for describing the shear stress in steady-state shear flows [BSL, §1.2 and §3.6; Bird et al., 1987a, Chapter 4]. But the non-Newtonian viscosity is not the only property that comes into play in polymer processing operations.

Even in steady-state shear flow ($v_x = \dot{\gamma} y$, $v_y = 0$, $v_z = 0$) the generalized Newtonian models do not describe the polymeric liquid behavior completely. It has been amply demonstrated experimentally that in steady-state shear flow, the normal stresses τ_{xx}, τ_{yy}, τ_{zz} are in general not zero and not equal to each other [Lodge, 1964, Chapter 10; Bird et al., 1987a, Chapters 2 and 3]. These normal stresses can be described by the *Criminale-Ericksen-Filbey equation* [BSL, Eq. 3.6-11; Bird et al., 1987a, Eq. 9.6-18]. But this equation is incapable of describing flows that are not steady-state shear flows.

To describe the time-dependent response of polymeric liquids in motions with infinitesimally small displacement gradients, one can make use of *linear viscoelastic models*. These are of the form:

$$\boldsymbol{\tau} + \lambda_1 \frac{\partial}{\partial t} \boldsymbol{\tau} + \mu_1 \frac{\partial^2}{\partial t^2} \boldsymbol{\tau} + \cdots = -\eta_0 \left(\dot{\boldsymbol{\gamma}} + \lambda_2 \frac{\partial}{\partial t} \dot{\boldsymbol{\gamma}} + \mu_2 \frac{\partial^2}{\partial t^2} \dot{\boldsymbol{\gamma}} + \cdots \right), \tag{78}$$

in which $\dot{\boldsymbol{\gamma}} = \nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger$ is the rate-of-deformation tensor, and the $+\cdots$ indicates that additional terms may be included, containing third and higher time derivatives. The λ_j, μ_j, $\cdots$ are constants characteristic of the fluid with dimensions of (time), (time)^2, $\cdots$, and η_0 is the zero-shear-rate viscosity. If all the constants but λ_1 are zero, the equation is the *Maxwell linear viscoelastic model*, and if all the constants save λ_1 and λ_2 are zero, we have the *Jeffreys linear viscoelastic model*. The latter can describe qualitatively stress relaxation after cessation of steady-state shear flow, stress growth at the start-up of shear flow, creep, recoil, and a variety of other unsteady-state responses--but only in motions that involve minuscule deformation gradients. Moreover, it cannot describe the strong dependence of the viscosity on the velocity gradients, nor can it describe the nonzero normal stresses in steady-state shear flow.

To describe all the rheological effects mentioned so far (non-Newtonian viscosity, normal stresses, and time-dependent responses) some success has been achieved by rewriting the linear viscoelastic models in a corotating frame (a frame that rotates with the local instantaneous angular velocity $\mathbf{w} = \frac{1}{2}[\nabla \times \mathbf{v}]$) and then transforming back to the fixed coordinate frame. When this is done for the Jeffreys model, we get

$$\boldsymbol{\tau} + \lambda_1 \frac{\mathcal{D}}{\mathcal{D}t} \boldsymbol{\tau} = -\eta_0 \left(\dot{\boldsymbol{\gamma}} + \lambda_2 \frac{\mathcal{D}}{\mathcal{D}t} \dot{\boldsymbol{\gamma}} \right), \tag{79}$$

which is the *corotational Jeffreys model*. Here the operator *D/Dt* is the corotational or "Jaumann" derivative, defined by

$$\frac{\mathcal{D}}{\mathcal{D}t} \boldsymbol{\tau} = \frac{D}{Dt} \boldsymbol{\tau} - \{\mathbf{w} \times \boldsymbol{\tau}\} - \{\mathbf{w} \times \boldsymbol{\tau}\}^\dagger, \tag{80}$$

for symmetrical $\boldsymbol{\tau}$. The reason for introducing the corotational derivatives is to insure that the resulting expression for the stress tensor will be "objective"--that is, it will have no unwanted dependence on the local rate of rotation in the fluid [Bird et al., 1977, Chapter 7]. Eq. (79) is found to have--qualitatively--most of the features needed for describing the rheological response of polymeric liquids, but the model is not sufficiently good quantitatively to be used in engineering flow calculations [Bird et al., 1977, §7.3]; however, in view of the fact that only three parameters are involved (a zero-shear-rate viscosity and two time constants), the development of Eq. (79) must be regarded with some satisfaction. In the past several decades many attempts have been made to generate--empirically--rheological equations containing the ideas of viscosity, elasticity, and objectivity, but which, with a small number of parameters, will be capable of quantitative fits of the available experimental data. Accounts of this quest have been given in a number of books, and no attempt is made here to discuss this extensive research field [Bird et al., 1987a, b; Larson, 1988; Giesekus, 1994; Bird and Wiest, 1996].

The above-described empirical development is a difficult task because we are dealing with the generation of tensor relations that must describe a very broad spectrum of rheological phenomena. In order to give some better sense of direction to the field, attempts have been made to use the kinetic theory to suggest likely forms for the tensor relations. We cite here just one example of an expression that comes from a nonlinear dumbbell model (the so-called "FENE-P model") which has received a lot of attention in the past decade as a reasonable subject for study in flow simulations. For a polymer solution at temperature T, in which the number density of polymer molecules is n, the stress tensor is given as the sum of a solvent contribution (the solvent viscosity being η_s) and a polymer contribution as follows:

$$\boldsymbol{\tau} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p = -\eta_s \dot{\boldsymbol{\gamma}} + \boldsymbol{\tau}_p, \tag{81}$$

in which, the polymer contribution is given by [Bird et al., 1987b, §13.5]

$$\begin{aligned} Z\boldsymbol{\tau}_p + \lambda_H \left(\frac{\mathcal{D}}{\mathcal{D}t} \boldsymbol{\tau}_p - \frac{1}{2} \{ \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\tau}_p + \boldsymbol{\tau}_p \cdot \dot{\boldsymbol{\gamma}} \} \right) \\ - \lambda_H (\boldsymbol{\tau}_p - nkT\boldsymbol{\delta}) \frac{D \ln Z}{Dt} = -nkT\lambda_H \dot{\boldsymbol{\gamma}}. \end{aligned} \tag{82}$$

Here $\lambda_H = \zeta/4H$ is a time constant, and $Z = 1 + (3/b)[1 - \mathrm{tr}(\boldsymbol{\tau}_p/3nkT)]$, where $b = HQ_0^2/kT$ is an "extensibility parameter". The "bead-spring" model parameters that enter into these quantities are: Q_0=maximum extension of the dumbbell, H=spring constant for the "spring", ζ=friction coefficient for a "bead" moving through the solvent. This equation contains a small number of adjustable parameters, each one of which has a specific molecular significance. If one uses Eq. (82) to solve a fluid dynamics problem, then one can get from the final results some additional information about molecular orientation and stretching.

In current research programs algorithms are being developed to solve the kinetic theory equations and the fluid dynamics equations simultaneously, using stochastic simulations for the kinetic theory and finite element methods for the fluid dynamics [Öttinger, 1996]. All of the subjects in this section are part of the frontier developments and are covered in the *Journal of Non-Newtonian Fluid Mechanics*, the *Journal of Rheology*, and *Rheologica Acta*.

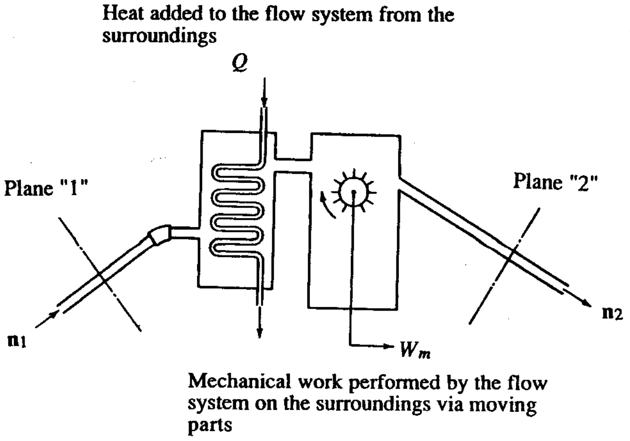


Fig. 6. A "macroscopic system", which may be all or a part of some large assembly of equipment. Application of conservation statements to this kind of system lead to the macroscopic, mass, momentum, angular momentum, and energy balances. The macroscopic mechanical energy balance, on the other hand, must be obtained by integrating the equation of change for mechanical energy over the entire system.

3. THE MACROSCOPIC VIEWPOINT

We now consider a macroscopic system such as that shown in Fig. 6. The system is the fluid contained between the inlet pipe ("1") with cross-sectional area S_1 and the outlet pipe ("2") with cross-sectional area S_2, the remainder of the surface being made up of fixed surfaces S_f; furthermore there may be moving surfaces S_m by means of which the system can do work on the surroundings at a rate W_m. Heat may be added to the system at a rate Q through some of the fixed surfaces of the system. The directions of flow at the inlet and outlet are given by the unit vectors $\mathbf{n}_1$ and $\mathbf{n}_2$. For the purpose of this discussion we consider the fluid in the system to be a single chemical species; it is not difficult to extend the discussion to multicomponent systems with chemical reactions [BSL, Chapter 22].

In establishing the macroscopic balances we make several assumptions:

a. Over the surfaces of the entrance and exit planes, it is assumed that the pressure, fluid density, internal energy, and potential energy do not vary.

b. It is assumed that in the entry and exit pipes the fluid is moving parallel to the walls of the pipe, so that the fluid velocity vectors (or the time-smoothed velocity vectors in turbulent flow) are in the directions $\mathbf{n}_1$ and $\mathbf{n}_2$ at the inlet and outlet respectively.

c. It is assumed that the contributions of the stress tensor τ and the heat-flux q vector at planes "1" and "2" may be neglected, because these quantities are normally small in comparison with other contributions.

3-1. Macroscopic Balances Based on Conservation Laws

When the above assumptions are made, it is possible to write down directly the following statements of the laws of conservation of mass, momentum, angular momentum, and total energy [BSL, Table 15.3-1]:

$$\frac{d}{dt}m_{tot} = w_1 - w_2 \tag{83}$$

$$\frac{d}{dt}\mathbf{P}_{tot} = \left(\frac{<v_1^2>w_1}{<v_1>} + p_1S_1\right)\mathbf{n}_1 - \left(\frac{<v_2^2>w_2}{<v_2>} + p_2S_2\right)\mathbf{n}_2 - \mathbf{F}_{f\rightarrow s} + m_{tot}\mathbf{g}, \tag{84}$$

$$\frac{d}{dt}\mathbf{L}_{tot} = \left(\frac{<v_1^2>w_1}{<v_1>} + p_1S_1\right)[\mathbf{r}_1\times\mathbf{n}_1] - \left(\frac{<v_2^2>w_2}{<v_2>} + p_2S_2\right)[\mathbf{r}_2\times\mathbf{n}_2] - \mathbf{T}_{f\rightarrow s} + [\mathbf{r}_c\times m_{tot}\mathbf{g}], \tag{85}$$

$$\frac{d}{dt}(K_{tot} + \Phi_{tot} + U_{tot}) = \left(\frac{1}{2}\frac{<v_1^3>}{<v_1>} + \hat{\Phi}_1 + \hat{H}_1\right)w_1 - \left(\frac{1}{2}\frac{<v_2^3>}{<v_2>} + \hat{\Phi}_2 + \hat{H}_2\right)w_2 + Q - W_m. \tag{86}$$

In these equations $w_1=\rho_1<v_1>S_1$ is the mass rate of flow at the entry plane, and a similar expression holds for the mass rate of flow at the exit plane. The quantities m_{tot}, $\mathbf{P}_{tot}$, $\mathbf{L}_{tot}$, K_{tot}, $\cdots$, are the total mass, linear momentum, angular momentum, kinetic energy, $\cdots$ in the system, and $\mathbf{g}=-\nabla\hat{\Phi}$ is the acceleration of gravity (taken to be unvarying with time). The vectors $\mathbf{F}_{f\rightarrow s}$ and $\mathbf{T}_{f\rightarrow s}$ are, respectively, the total force and total torque exerted by the fluid (f) on the solid (s) surfaces. The angular brackets imply averages over the cross-sections at the inlet and exit planes, and these averages arise because of the variation of the fluid velocity over the cross-section. The position vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_c$ give the locations of the centers of the entrance and exit planes and the location of the center of mass of the system; the terms containing the position vectors are only approximate, inasmuch as these vectors are not included in the relevant averaging processes.

These macroscopic balances can be written down directly by applying the conservation laws, but they can also be obtained by integrating the corresponding equations of change over the entire volume of the flow system, taking into account the fact that the volume of the system is changing with time, because of the inclusion of moving mechanical parts. [Bird, 1957; Slattery and Gaggioli, 1962]. We do not gives these derivations here, but, instead, illustrate the procedure in connection with the derivation of the mechanical energy balance in the next subsection.

3-2. The Macroscopic Mechanical Energy Balance

A macroscopic mechanical energy balance cannot be written down immediately, since it does not follow from a conservation law. Instead, we begin with the equation of change for mechanical energy and integrate it over the flow system of Fig. 6 [Bird, 1957, 1993; Whitaker, 1989, pp. 90-93].

We start by rewriting the equation of change for mechanical energy (Eq. (49)) for a pure fluid in the $\partial/\partial t$-form and by introducing the potential energy per unit mass $\hat{\Phi}$ defined by the relation $\mathbf{g}=-\nabla\hat{\Phi}$. It is assumed that $\hat{\Phi}$ is time-independent, so that the equation of continuity may be used to rewrite the mechanical energy equation as follows:

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho v^2+\rho\hat{\Phi}\right)=-\left(\nabla\cdot\left(\frac{1}{2}\rho v^2+\rho\hat{\Phi}\right)\mathbf{v}\right)-(\nabla\cdot[\boldsymbol{\pi}\cdot\mathbf{v}])+(\boldsymbol{\pi}:\nabla\mathbf{v}). \tag{87}$$

We now want to integrate this equation over the entire volume of a flow system. To do this, two integral theorems are needed, the Gauss divergence theorem for any vector function **A** (x, y, z, t) and the Leibniz formula for differentiation of a three-dimensional integral of a scalar function f (x, y, z, t) [BSL, Eqs. (A.5-1) and (A.5-5)]:

$$\text{Gauss: } \int_{V(t)}(\nabla\cdot\mathbf{A})dV=\int_{S(t)}(\mathbf{n}\cdot\mathbf{A})dS, \tag{88}$$

$$\text{Leibniz: } \frac{d}{dt}\int_{V(t)}f(x,y,z,t)dV=\int_{V(t)}\frac{\partial f}{\partial t}dV+\int_{S(t)}f(\mathbf{n}\cdot\mathbf{v}_S)dS, \tag{89}$$

in which V(t) and S(t) are the volume and surface of the system, which may depend on time because of the moving parts, and $\mathbf{v}_S$ is the local velocity of that part of the surface which is moving.

When Eq. (87) is integrated, the three-dimensional Leibniz formula is used on the first term and the divergence terms are converted to surface integrals, and we get

$$\frac{d}{dt}\int_{V(t)}\left(\frac{1}{2}\rho v^2+\rho\hat{\Phi}\right)dV=-\int_{S(t)}\left(\mathbf{n}\cdot\left(\frac{1}{2}\rho v^2+\rho\hat{\Phi}\right)(\mathbf{v}-\mathbf{v}_S)\right)dS-\int_{S(t)}(\mathbf{n}\cdot[\boldsymbol{\pi}\cdot\mathbf{v}])dS+\int_{V(t)}(\boldsymbol{\pi}:\nabla\mathbf{v})dV, \tag{90}$$

The surface S(t) consists of four surfaces: the fixed surfaces S_f, on which both **v** and $\mathbf{v}_S$ are zero; the moving surfaces S_m, on which $\mathbf{v}=\mathbf{v}_S$, both being nonzero; the cross-sections of the entry and exit ports, S_1 and S_2, where $\mathbf{v}_S$ is zero, but not **v**.

The term on the left of Eq. (90) becomes the time rate of change of the total kinetic and potential energies ($K_{tot}+\Phi_{tot}$) within the control volume, whose shape and volume are in general changing with time. We next consider seriatim the three terms on the right: Term (1) contributes only at the entry and exit ports, and this gives the influx and efflux of kinetic and potential energy $\left(\frac{1}{2}\rho_1<v_1^3>S_1+\rho_1<v_1>\hat{\Phi}_1 S_1\right)$ and $-\left(\frac{1}{2}\rho_2<v_2^3>S_2+\rho_2<v_2>\hat{\Phi}_2 S_2\right)$. The angular brackets indicate averages over the cross-sections, and the subscripts "1" and "2" show that the quantities are evaluated at planes "1" and "2". Term (2) gives, at the entry and exit ports, the work done to force the fluid into the system and to force the fluid out of the system; it is customary to neglect the viscous forces and include here only the pressure forces, so that this term gives rise to the terms $p_1<v_1>S_1$ and $-p_2<v_2>S_2$. Term (2) gives no contribution on the fixed surfaces, but on the moving surfaces gives the rate of work done on the surroundings by means of the moving parts W_m. Term (3) may be split up into two parts--the part associated with the pressure, and that associated with the viscous forces--and these are given symbolic designations:

$$E_c=-\int_{V(t)}(p\boldsymbol{\delta}:\nabla\mathbf{v})dV=-\int_{V(t)}p(\nabla\cdot\mathbf{v})dV, \tag{91}$$

$$E_v=-\int_{V(t)}(\boldsymbol{\tau}:\nabla\mathbf{v})dV, \tag{92}$$

The quantity E_v is the rate of dissipation of mechanical energy within the control volume and, for Newtonian fluids, is always positive, whereas E_c may be either positive or negative; however, E_c can be discarded if the assumption of incompressibility is made.

When these various contributions are inserted into Eq. (90), we get finally for the *macroscopic mechanical energy balance*

$$\frac{d}{dt}(K_{tot}+\Phi_{tot})=\left(\frac{1}{2}\rho_1<v_1^3>S_1+\rho_1<v_1>\hat{\Phi}_1 S_1+p_1<v_1>S_1\right)-\left(\frac{1}{2}\rho_2<v_2^3>S_2+\rho_2<v_2>\hat{\Phi}_2 S_2+p_2<v_2>S_2\right)-W_m-E_c-E_v, \tag{93}$$

or

$$\frac{d}{dt}(K_{tot}+\Phi_{tot})=\left(\frac{1}{2}\frac{<v_1^3>}{<v_1>}+\hat{\Phi}_1+\frac{p_1}{\rho_1}\right)w_1-\left(\frac{1}{2}\frac{<v_2^3>}{<v_2>}+\hat{\Phi}_2+\frac{p_2}{\rho_2}\right)w_2-W_m-E_c-E_v. \tag{94}$$

This is sometimes referred to as the *engineering Bernoulli equation* or the *overall mechanical energy balance.* This equation is used together with the overall mass, momentum, angular momentum, and total energy balances for analyzing engineering flow systems [BSL, Chapters 7 and 15; Whitaker, 1968; Bird, 1993]. The form of the mechanical energy balance give in Eq. (94) is much to be preferred over those given in BSL, Eqs. 15.2-1 and 2; if the fluid can be regarded as incompressible, the term E_c may be discarded, as pointed out above.

If the macroscopic mechanical energy balance in Eq. (94) is subtracted from the total energy balance in Eq. (90), a macroscopic internal energy balance is obtained:

$$\frac{d}{dt}U_{tot}=\hat{U}_1 w_1-\hat{U}_2 w_2+Q+E_c+E_v \tag{95}$$

This equation, which is an interesting relation among thermal quantities, cannot be written down immediately, inasmuch as there is no law of conservation of internal energy.

It is clear from the derivation above that Eq. (94) is obtained from the law of conservation of momentum. In some textbooks it is stated (incorrectly) that the mechanical energy balances is "an alternative form of the total energy balance"; indeed, some textbook authors have obtained Eq. (94) by subtracting Eq. (95) from the total energy balance in Eq. (90), failing to recognize that Eq. (95) cannot be written down from first principles.

3-3. The Macroscopic Balances for Steady-State Systems

Frequently the macroscopic balances are simplified by assuming time-independent flows and neglecting the change of velocity over the cross-sections at "1" and "2". At the same time, it is convenient to generalize the balances by allowing for multiple entry and exit ports. We then get the following for the four conservation statements and the mechanical energy balance:

$$\Sigma \mathrm{w}_1 - \Sigma \mathrm{w}_2 = 0, \tag{96}$$

$$\Sigma(\mathrm{v}_1\mathrm{w}_1 + \mathrm{p}_1\mathrm{S}_1)\mathbf{n}_1 - \Sigma(\mathrm{v}_2\mathrm{w}_2 + \mathrm{p}_2\mathrm{S}_2)\mathbf{n}_2 + \mathrm{m}_{tot}\,\mathbf{g} = \mathbf{F}_{f\to s}, \tag{97}$$

$$\begin{aligned}\Sigma(\mathrm{v}_1\mathrm{w}_1 + \mathrm{p}_1\mathrm{S}_1)[\mathbf{r}_1 \times \mathbf{n}_1] - \Sigma(\mathrm{v}_2\mathrm{w}_2 + \mathrm{p}_2\mathrm{S}_2)[\mathbf{r}_2 \times \mathbf{n}_2]\\ +[\mathbf{r}_c \times \mathrm{m}_{tot}\,\mathbf{g}] = \mathbf{T}_{f\to s},\end{aligned} \tag{98}$$

$$\Sigma\left(\frac{1}{2}\mathrm{v}_1^2 + \mathrm{gh}_1 + \hat{\mathrm{H}}_1\right)\mathrm{w}_1 - \Sigma\left(\frac{1}{2}\mathrm{v}_2^2 + \mathrm{gh}_2 + \hat{\mathrm{H}}_2\right)\mathrm{w}_2 + \mathrm{Q} - \mathrm{W}_m = 0 \tag{99}$$

$$\begin{aligned}\Sigma\left(\frac{1}{2}\mathrm{v}_1^2 + \mathrm{gh}_1 + (\mathrm{p}_1/\rho_1)\right)\mathrm{w}_1 - \Sigma\left(\frac{1}{2}\mathrm{v}_2^2 + \mathrm{gh}_2 + (\mathrm{p}_2/\rho_2)\right)\mathrm{w}_2\\ -\mathrm{W}_m - \mathrm{E}_c - \mathrm{E}_v = 0.\end{aligned} \tag{100}$$

Here $\Sigma \mathrm{w}_1$ means a sum over all entry ports of the mass flow rates; h_1 is the height of the entry port above some arbitrarily chosen datum plane. The enthalpy that appears in Eq. (99) is obtained from the following equation:

$$\hat{\mathrm{H}} - \hat{\mathrm{H}}^0 = \int_{T^0}^{T} \hat{\mathrm{C}}_p\,\mathrm{dT} + \int_{p^0}^{p}\left(\hat{\mathrm{V}} - \mathrm{T}\left(\frac{\partial \hat{\mathrm{V}}}{\partial \mathrm{T}}\right)_p\right)\mathrm{dp}, \tag{101}$$

in which the symbols with a superscript "0" refer to an arbitrary reference state. The integration paths must prescribed, since each integral may depend on both p and T.

Eqs. (96) through (100) constitute a set of five equations which have to be solved simultaneously. Most textbooks (including BSL) do not emphasize sufficiently that the use of this set of equations usually requires some intuition (to decide which terms are important and which ones can be safely neglected), some additional information (such as heat-transfer coefficients or friction factors), and perhaps some photographs or flow visualization in order to decide which terms may be safely neglected, or to estimate their value.

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