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CHEMICAL ENGINEERING EDUCATION: MAKING CONNECTIONS AT INTERFACES

EDUCACIÓN EN INGENIERÍA QUÍMICA: HACIENDO CONEXIONES EN INTERFACES

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Abstract

An interface may be a region in which *concepts* are connected, or it may be a region in which *physical processes* are connected. In both cases, conditions change abruptly. In this study, the interface between physics and chemical engineering is examined from the point of view of the laws of mechanics, and the details of this particular interface are clarified from the perspective of Euler (1703-1783) and Cauchy (1789-1857). Understanding how different perspectives of the laws of mechanics are *connected* allows us to proceed with confidence from physics to the traditional studies of fluid mechanics that one encounters in chemical engineering. Furthermore, it allows us to proceed with confidence to the study of multi-component transport phenomena. Here we encounter the concept of the *species velocity* that plays a crucial role in chemical engineering. To understand the importance of the species velocity, one asks the question: What happens if all species velocities are equal? The answer to this question is: Nothing! There is no purification, no mixing, no interfacial mass transfer, no adsorption/desorption, no homogeneous reaction, and no heterogeneous reaction. To illustrate how the concepts of mechanics provide a *connection* between various elements of chemical engineering, we examine the species mass jump condition as a *focal point* for mass transfer, heat transfer, thermodynamics, adsorption/desorption, and heterogeneous chemical reaction.

Keywords: Newton, Euler, Cauchy, multicomponent systems, phase interfaces.

Resumen

Una interface puede ser una región en la cual se conectan *conceptos*, o puede ser una región en la cual se conectan *procesos físicos*. En ambos casos, las condiciones cambian abruptamente. En este estudio, la interface entre la física y la ingeniería química es examinada desde el punto de vista de las leyes de la mecánica, y los detalles de esta interface particular son aclarados desde la perspectiva de Euler (1703-1783) y Cauchy (1789-1857). El entender cómo diferentes perspectivas de las leyes de la mecánica están *conectadas* nos permite proceder con confianza desde la física hasta los estudios tradicionales de mecánica de fluidos que uno encuentra en ingeniería química. Más aún, nos permite proceder con certidumbre en el estudio de fenómenos de transporte multi-componentes. Aquí encontramos el concepto de *velocidad de especie* que juega un papel crucial en ingeniería química. Para entender la importancia de la velocidad de especies, se hace la pregunta: ¿Qué sucede si las velocidades de todas las especies son iguales? La respuesta a esta pregunta es: ¡Nada! No hay purificación, mezclado, transferencia de masa interfacial, ni adsorción/desorción, ni reacción homogénea, y no hay reacción heterogénea. Para ilustrar como los conceptos de la mecánica proporcionan una *conexión* entre los diferentes elementos de la ingeniería química, examinamos la condición de salto de especies de masa como un *punto focal* para la transferencia de masa, transferencia de calor, termodinámica, adsorción/desorción, y reacción química heterogénea.

Palabras clave: Newton, Euler, Cauchy, sistemas multicomponentes, interfaces entre fases.

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Contents

1. Physics and Chemical Engineering

Most chemical engineering programs are preceded by a series of courses in physics, mathematics, and chemistry. In addition, courses in other disciplines such as biology, ecology, economics, etc., are often taken simultaneously. Knowledge of these other disciplines can often be crucial to chemical engineering students who are notorious for their breadth of professional activities. In each of these other disciplines, one encounters a certain culture that generally creates an abrupt change with the culture one finds in chemical engineering. This cultural change represents an interface that can be difficult to negotiate for a chemical engineering student. To illustrate this type of abrupt change between one discipline and another, we consider the discipline of physics and within that discipline we consider the subject of mechanics.

1.1 Newton's laws

In order to develop the governing equations for the fluid velocity, and more importantly for the *species velocity*, we need a clear understanding of the laws of physics that govern that motion. Courses in physics present Newton's laws and use them to determine the motion of *mass points* and *rigid bodies*. Truesdell (1968, page 88) tells us that Newton listed his three laws of motion as:

<u>Newton</u> (1642-1727)

I. Every body continues in its state of rest, or of uniform motion straight ahead, unless it be compelled to change that state by forces impressed upon it.

II. The change of motion is proportional to the motive force impressed, and it takes place along the right line in which the force is impressed.

III. To an action there is always a contrary and equal reaction; or, the mutual actions of two bodies upon each other are always directed to contrary parts.

Truesdell (1968, page 167) also tells us that Newton never presented these ideas in the form of equations and because of this there are differences to be found in the literature. Here we choose "motion" to mean mass times velocity, $m\mathbf{v}$, and we choose "motive force" to be represented by $\mathbf{f}$. This leads to the first law given by

$$\text{Newton I:} \qquad m\mathbf{v} = \text{constant}, \quad \mathbf{f} = 0 \tag{1}$$

while the second law takes the form

$$\text{Newton II:} \qquad \frac{d}{dt}\left(m\,\mathbf{v}\right) = \mathbf{f} \tag{2}$$

Here the "change of motion" has been interpreted as the time rate of change of the momentum, $m\mathbf{v}$. Often a precise definition of $\mathbf{v}$ is not given in the discussion of Newton's first and second laws, and we will return to this matter in subsequent paragraphs. Clearly Newton's first law is a special case of Newton's second law, and one can wonder why it was stated as an independent law. Physicists (Feyman *et al.*, 1963, Vol I, page 9-1; Huggins, 1968, page 109; Greider, 1973, page 38) have pointed out that Eq. (1) was deduced earlier by Galileo (1564-1642), thus Newton was motivated to elevate this result to the position of a "law".

Newton's third law for two interacting bodies can be expressed as

$$\text{Newton III:} \qquad \mathbf{f}_{12} = -\,\mathbf{f}_{21} \tag{3}$$

in which $\mathbf{f}_{12}$ is the force that body #2 exerts on body #1, and $\mathbf{f}_{21}$ is the force that body #1 exerts on body #2. The most dramatic success of these laws was their use, along with the *law of gravitational attraction*, to justify Kepler's three empirical laws of planetary motion. In a careful statement of Newton's laws, one often notes that they are valid in an *inertial frame*. This naturally leads to the question: What is an inertial frame? The answer is that an inertial frame is a frame in which Newton's laws are valid! We can only escape from this circular argument by noting that an inertial frame must be determined by experiment (Hurley and Garrod, 1978, page 49). In Newton's case, the verification of Kepler's laws indicated that the sun and the "fixed stars" represented a *good approximation* of an inertial frame for the study of planetary motion.

If we think about applying Eq. (2) to the motion of a body, we must wonder what is meant by the velocity $\mathbf{v}$, since all parts of a body need not have the same velocity. Physicists often deal with this problem by arguing that Eq. (2) applies to "mass points" that are small enough so that their motion can be described by a single velocity. The statement that something is "small" always leads to the question: Small relative to what? Feynman *et al.* (1963, Vol I, page 18-1) touch on this problem by considering the cloud of N mass points illustrated in Fig. 1. One can apply Newton's second law to the i th mass point in the cloud in order to obtain

$$\frac{d}{dt}\left(m_i\mathbf{v}_i\right) = \mathbf{b}_i + \sum_{j=1}^{j=N}\mathbf{f}_{ij} \tag{4}$$

Here we have used $\mathbf{b}_i$ to represent the force exerted on the i th mass point by the large, spherical body located outside the cloud in Fig. 1. The force exerted by the j th mass point in the cloud on the i th mass point in the cloud is represented by $\mathbf{f}_{ij}$, and this force obeys Newton's third law as indicated by

$$\mathbf{f}_{ij} = -\,\mathbf{f}_{ji} \tag{5}$$

To obtain Newton's second law for the cloud of mass points, we sum Eq. (4) over all the mass points in the cloud (Marion, 1970, page 68)

$$\frac{d}{dt}\sum_{i=1}^{i=N} m_i\mathbf{v}_i = \sum_{i=1}^{i=N}\mathbf{b}_i + \sum_{i=1}^{i=N}\sum_{j=1}^{j=N}\mathbf{f}_{ij} \tag{6}$$

and make use of Eq. (5) to simplify this result to the form

$$\frac{d}{dt}\sum_{i=1}^{i=N} m_i\mathbf{v}_i = \sum_{i=1}^{i=N}\mathbf{b}_i \tag{7}$$

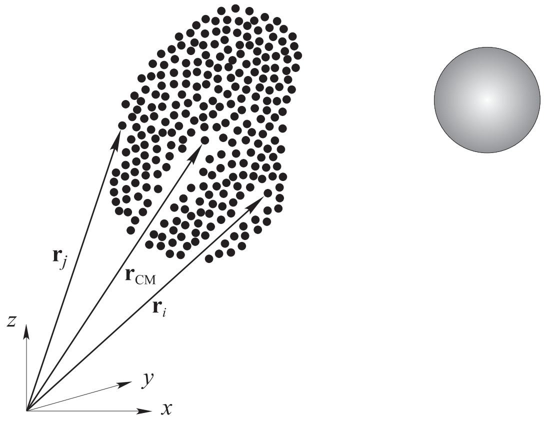

Fig. 1. Cloud of mass points interacting with a body.

The mass of the cloud is given by

$$m = \sum_{i=1}^{i=N} m_i \tag{8}$$

while the center of mass, $\mathbf{r}_{\rm CM}$, and the velocity of the center of mass, $\mathbf{v}_{\rm CM}$, are defined by

$$\mathbf{r}_{\rm CM} = \frac{1}{m}\sum_{i=1}^{i=N} m_i\,\mathbf{r}_i\,, \qquad \mathbf{v}_{\rm CM} = \frac{1}{m}\sum_{i=1}^{i=N} m_i\,\mathbf{v}_i \tag{9}$$

The second of these definitions allows us to express Eq. (7) in the form

$$\frac{d}{dt}\left(m\,\mathbf{v}_{\rm CM}\right) = \sum_{i=1}^{i=N} \mathbf{b}_i \tag{10}$$

We now identify the total external force acting on the cloud of mass points as

$$\mathbf{f} = \sum_{i=1}^{i=N} \mathbf{b}_i \tag{11}$$

so that Newton's second law for a cloud of mass points is given by

$$\text{Newton II:} \qquad \frac{d}{dt}\left(m\,\mathbf{v}_{\rm CM}\right) = \mathbf{f} \tag{12}$$

Feynman *et al.*(1963, Vol I, page 19-2) describe this situation by saying "Newton's law has the peculiar property that if it is right on a certain scale [*the mass point scale*], then it will be right on a larger scale [*the cloud scale*]." While this is a satisfying result, it does not explain "how small" a particle must be in order that Eq. (2) can be applied with confidence. For rigid bodies the velocity **v** at any point **r** is given by (Landau and Lifshitz, 1960)

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_{\rm CM} + \boldsymbol{\omega}\times\left(\mathbf{r}-\mathbf{r}_{\rm CM}\right) \tag{13}$$

in which $\boldsymbol{\omega}$ represents the angular velocity. Here we see that a *single velocity* can be used to describe the motion of a rigid body whenever $\boldsymbol{\omega}$ x ($\mathbf{r} - \mathbf{r}_{\rm CM}$) is small compared to $\mathbf{v}_{\rm CM}$, thus the constraint associated with the "mass point" assumption is given by

$$\text{Constraint:} \qquad \boldsymbol{\omega}\times(\mathbf{r}-\mathbf{r}_{\rm CM}) \ll \mathbf{v}_{\rm CM} \tag{14}$$

For deformable bodies, one must replace Eq. (13) with the more general representation

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_{\rm CM} + \int_{\boldsymbol{\eta}=\mathbf{r}_{\rm CM}}^{\boldsymbol{\eta}=\mathbf{r}} \left(\nabla\mathbf{v}\right)^{\rm T}\cdot d\boldsymbol{\eta} \tag{15}$$

and then examine the velocity gradient tensor in terms of it symmetric and skew-symmetric parts (Aris, 1962, page 89). In this case, the *restriction* (Whitaker, 1988) is obviously given by

$$\text{Restriction:} \qquad \int_{\boldsymbol{\eta}=\mathbf{r}_{\rm CM}}^{\boldsymbol{\eta}=\mathbf{r}} \left(\nabla\mathbf{v}\right)^{\rm T}\cdot d\boldsymbol{\eta} \ll \mathbf{v}_{\rm CM} \tag{16}$$

however, the associated *constraint* would require a detailed analysis of the fluid deformation. If one accepts Eq. (12) as Newton's second law instead of Eq. (2), no constraint need be imposed.

Momentum balance

While Eqs. (1) through (12) represent a reasonable beginning for the study of mechanics, Newton's three laws are difficult to apply to the motion of a fluid. Because of this, chemical engineering texts often present a *completely new statement* of the laws of mechanics. This new statement is known as the *macroscopic momentum balance* which can be expressed as

$$\begin{Bmatrix} \text{rate of } \textit{accumulation} \\ \text{of linear momentum} \\ \text{in the control volume} \end{Bmatrix} + \begin{Bmatrix} \textit{flux} \text{ of linear} \\ \text{momentum leaving} \\ \text{the control volume} \end{Bmatrix} - \begin{Bmatrix} \textit{flux} \text{ of linear} \\ \text{momentum entering} \\ \text{the control volume} \end{Bmatrix} = \begin{Bmatrix} \text{forces acting} \\ \text{on the} \\ \text{control volume} \end{Bmatrix} \tag{17}$$

While this result is relatively easy to apply, it represents a leap of faith (Whitaker, 1999) from what students have learned in their study of physics. In the absence of an explanation, the momentum balance becomes a recipe to be used under conditions identified in a text book as opposed to a tool to be used as one wishes. The work of Euler (1703-1783) and Cauchy (1789-1857) provides a *connection* between Newton's laws and the macroscopic momentum balance, and we outline this connection in the following paragraphs.

1.2 Euler's laws

While Newton's laws seem to be suitable for the study of mass points and clouds of mass points, they cannot be applied directly to the motion of a moving, deforming, continuous medium (Serrin, 1959, page 134). Regardless of what words are used to describe the laws of mechanics used by chemical engineers, those laws are indeed the laws proposed by Euler (1707-1783) that can be stated as

Euler (1707-1783)

I. The time rate of change of the momentum of a body equals the force acting on the body.

II. The time rate of change of the angular momentum of a body equals the torque acting on the body, where both the torque and the moment are taken with respect to the same fixed point.

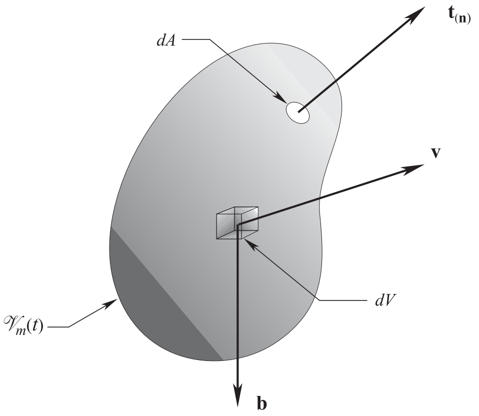

Fig. 2. Moving, deforming body.

In addition to these two laws, we accept the *Euler cut principle* (Truesdell, 1968, page 193) stated as:

> Not only do the laws of continuum physics apply to *distinct bodies* but they also apply to any arbitrary body that one might imagine as being *cut out* of a distinct body.

Associated with this concept is the idea that the velocity at a point can be thought of as the average velocity of the molecules in the neighborhood of that point. If the length scale associated with that neighborhood is *small* compared to the characteristic length of the system under consideration, the *continuum model* should provide an accurate representation. If the characteristic length of the system under consideration is *not small* compared to the average distance between molecules, one must deal with the mechanics of molecular motion (Tolman, 1938).

In order to understand how Euler's laws are related to Newton's laws, we need to put Euler's laws in precise mathematical form. This will allow us to demonstrate that they *contain* Newton's laws provided that we restrict ourselves to *non-relativistic phenomena*. Since Euler's two laws and the Euler cut principle form the basis for virtually all of engineering mechanics, it is important that we understand these concepts.

We begin our study of Euler's laws by expressing them in terms of the following two equations

$$\left\{\begin{matrix}\text{time rate of change}\\ \text{of the linear momentum}\\ \text{of a } \textit{body}\end{matrix}\right\} = \left\{\begin{matrix}\text{force acting on}\\ \text{the } \textit{body}\end{matrix}\right\} \tag{18}$$

$$\left\{\begin{matrix}\text{time rate of change}\\ \text{of the angular}\\ \text{momentum of a } \textit{body}\end{matrix}\right\} = \left\{\begin{matrix}\text{torgue acting on}\\ \text{the } \textit{body}\end{matrix}\right\} \tag{19}$$

to which we add the non-relativistic concept that the mass of a *body* is a constant.

$$\left\{\begin{matrix}\text{time rate of change}\\ \text{of the mass of a } \textit{body}\end{matrix}\right\} = 0 \tag{20}$$

In Fig. 2 we have illustrated an *arbitrary body* that one can image as being cut out of a *distinct body*. The volume of this *moving*, *deforming body* is designated as $\mathscr{V}_m(t)$, and the differential volume and surface elements are identified as dV and dA respectively. The vector force *per unit surface area* is designated by the *stress vector*, $\mathbf{t}_{(\mathbf{n})}$ which represents a *contact force* that the *surroundings exert on the body*. The vector force *per unit mass* is designated by $\mathbf{b}$ and it represents a force *acting at a distance* that is exerted *on the body*. For many processes, the force per unit mass is equal to the gravitational acceleration, i.e., $\mathbf{b} = \mathbf{g}$; however, this simplification is only valid when the electrodynamic and electromagnetic forces are negligible.

We begin our analysis of Eq. (18) by constructing a mathematical representation of the momentum of the body. The mass, dm, contained in the differential volume element shown in Fig. 2 is given by

$$dm = \rho\, dV \tag{21}$$

and the momentum (mass times velocity) per unit volume takes the form

$$\mathbf{v}\, dm = \rho\, \mathbf{v}\, dV \tag{22}$$

The total momentum of the body is the volume integral of this quantity, and we express this as

$$\left\{\begin{matrix}\text{momentum}\\ \text{of the body}\end{matrix}\right\} = \int\limits_{\mathscr{V}_m(t)} \rho\, \mathbf{v}\, dV \tag{23}$$

which allows us to express the first term in Eq. (18) in the form

$$\frac{d}{dt}\int\limits_{\mathscr{V}_m(t)} \rho\, \mathbf{v}\, dV = \left\{\begin{matrix}\text{time rate of change}\\ \text{of the linear momentum}\\ \text{of a } \textit{body}\end{matrix}\right\} \tag{24}$$

To complete our mathematical representation of Eq. (18), we need to express the force acting on the body in terms of the *body force* and the *surface force*. The first of these is given by

$$\left\{\begin{matrix}\text{body force acting}\\ \text{on the body}\end{matrix}\right\} = \int\limits_{\mathscr{V}_m(t)} \rho\, \mathbf{b}\, dV \tag{25}$$

while the second takes the form

$$\left\{\begin{matrix}\text{surface force acting}\\ \text{on the body}\end{matrix}\right\} = \int\limits_{\mathscr{A}_m(t)} \mathbf{t}_{(\mathbf{n})}\, dA \tag{26}$$

Use of Eqs. (24), (25) and (26) in the word equation given by Eq. (18) leads to a precise mathematical statement of Euler's first law.

$$\text{Euler I}: \quad \frac{d}{dt}\int\limits_{\mathscr{V}_m(t)} \rho\, \mathbf{v}\, dV = \int\limits_{\mathscr{V}_m(t)} \rho\, \mathbf{b}\, dV + \int\limits_{\mathscr{A}_m(t)} \mathbf{t}_{(\mathbf{n})}\, dA \tag{27}$$

Following this same type of analysis, one can show that the word equation given by Eq. (19) takes the form[1]

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[1] Here all torques are the moments of forces, thus *body torques* have been ignored (Serrin, 1959, Dahler and Scriven, 1961; Aris, 1962).

$$\text{Euler II}: \frac{d}{dt}\int_{\mathscr{V}_m(t)} \mathbf{r}\times\rho\mathbf{v}\,dV = \int_{\mathscr{V}_m(t)} \mathbf{r}\times\rho\mathbf{b}\,dV + \int_{\mathscr{A}_m(t)} \mathbf{r}\times\mathbf{t}_{(\mathbf{n})}\,dA \tag{28}$$

To be precise about Euler's two laws, we need to say that the velocity, **v**, is determined relative to an *inertial frame* and that the position vector **r** is determined relative to some fixed point in an inertial frame. As mentioned earlier in connection with Newton's laws, one identifies an inertial frame by experiment. In addition to the precise statement of Euler's two laws of mechanics, we need a similar statement for the principle of conservation of mass. Integration of Eq. (21) over the volume occupied by a body yields the mass of the body, and this result can be used with Eq. (20) to obtain

$$\text{Mass:} \qquad \frac{d}{dt}\int_{\mathscr{V}_m(t)} \rho\,dV = 0 \tag{29}$$

It is important to remember that these three axiomatic statements for *linear momentum*, *angular momentum* and *mass* apply to any *arbitrary body* that one imagines as being cut out of a distinct body.

1.3 Euler's laws and Newton's laws

Given Euler's two laws of mechanics and the Euler cut principle, we need to know how they are related to Newton's three laws. To explore this problem, we consider a body of mass *m* illustrated in Fig. 3, and we locate the *center of mass* of that body in terms of the position vector *defined* by

$$\mathbf{r}_{\mathrm{CM}} = \frac{1}{m}\int_{\mathscr{V}_m(t)} \rho\,\mathbf{r}\,dV \tag{30}$$

This definition of the center of mass for a body is analogous to the definition for a cloud of mass points given earlier by the first of Eqs. (9). For a sphere of uniform density, the center of mass would be located at the geometrical center of the sphere; however, the definition of $\mathbf{r}_{\mathrm{CM}}$ is completely general and Eq. (30) is applicable to *any arbitrary body* that is *cut out of* a distinct body. The velocity of the center of mass is *defined* in a similar manner

$$\mathbf{v}_{\mathrm{CM}} = \frac{1}{m}\int_{\mathscr{V}_m(t)} \rho\,\mathbf{v}\,dV \tag{31}$$

and one can use a special form of the Reynolds transport theorem (Whitaker, 1981, page 94) to prove that

$$\mathbf{v}_{\mathrm{CM}} = \frac{d\,\mathbf{r}_{\mathrm{CM}}}{dt} \tag{32}$$

The definition given by Eq. (31) can be used to express the first term in Eq. (27) as

$$\frac{d}{dt}\int_{\mathscr{V}_m(t)} \rho\,\mathbf{v}\,dV = \frac{d}{dt}\left(m\,\mathbf{v}_{\mathrm{CM}}\right) \tag{33}$$

As a matter of convenience, we designate the total force acting on the body by

$$\mathbf{f} = \int_{\mathscr{V}_m(t)} \rho\,\mathbf{b}\,dV + \int_{\mathscr{A}_m(t)} \mathbf{t}_{(\mathbf{n})}\,dA \tag{34}$$

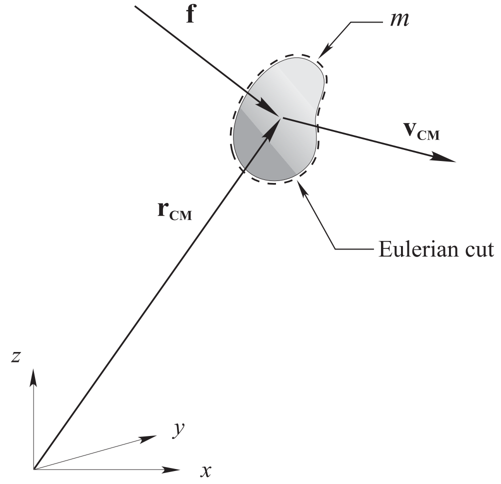

Fig. 3. Motion of a body.

so that Eq. (27) can be represented in the simplified form given by

$$\text{Euler Result I:} \qquad \frac{d}{dt}\left(m\,\mathbf{v}_{\mathrm{CM}}\right) = \mathbf{f} \tag{35}$$

This is identical in form to Newton's second law for the cloud of mass points illustrated in Fig. 1, and if the body is "small enough" so that $\mathbf{v}_{\mathrm{CM}}$ can be replaced by **v** we see that Eq. (35) is identical in form to Eq. (2) for a mass point. In addition, one can certainly imagine that the force in Eq. (2) includes both a *body force* and a *surface force* and this would be consistent with the representation given by Eq. (34). However, if one accepts this point of view, one must be careful to indicate that Newton's third law given by Eq. (3) only applies to *body forces*. The similarity in form (*not content*) of Euler's first law and Newton's second law has encouraged many to think that Newton's laws and Euler's first law are essentially equivalent. This is a line of thought that should be discouraged since Newton's laws cannot be applied directly to the motion of a moving, deforming, continuous medium (Serrin, 1959, page 134). Thus fluid motion and the deformation of solids are processes that are beyond the reach of Newton's laws as given by Eqs. (1) through (3).

Body forces

In order to clarify the different perspectives of physicists and chemical engineers, we apply Euler's first and second laws to the special case of three interacting bodies in a vacuum[2]. This situation is illustrated in Fig. 4 where we have shown two distinct small bodies, three Eulerian cuts and a distinct large body. For Cut I and Cut II, Euler's first law yields

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[2]. In this section we have omitted surface forces in order to simplify the analysis. In Appendix A we show that the inclusion of surface forces does not alter the result obtained here.

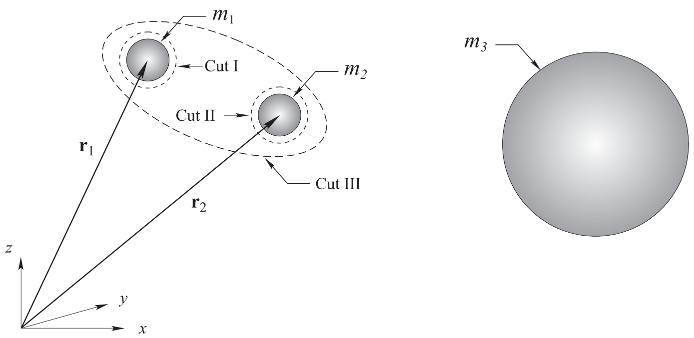

Fig. 4. Three-body process.

$$\text{Cut I}: \frac{d}{dt}\int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \rho_1\,\mathbf{v}_1\,dV = \int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \rho_1\,\mathbf{b}_{12}\,dV + \int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \rho_1\,\mathbf{b}_{13}\,dV \tag{36}$$

$$\text{Cut II}: \frac{d}{dt}\int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \rho_2\,\mathbf{v}_2\,dV = \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \rho_2\,\mathbf{b}_{21}\,dV + \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \rho_2\,\mathbf{b}_{23}\,dV \tag{37}$$

The application of Cut III treats the two small bodies as a single body for which the time rate of change of momentum is balanced by the applied external force. This leads to

$$\begin{aligned}\text{Cut III}: \ &\frac{d}{dt}\left[\int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \rho_1\,\mathbf{v}_1\,dV + \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \rho_2\,\mathbf{v}_2\,dV\right]\\ &= \int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \rho_1\,\mathbf{b}_{13}\,dV + \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \rho_2\,\mathbf{b}_{23}\,dV\end{aligned} \tag{38}$$

Substitution of Eqs. (36) and (37) into Eq. (38) provides

$$\int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \rho_1\,\mathbf{b}_{12}\,dV + \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \rho_2\,\mathbf{b}_{21}\,dV = 0 \tag{39}$$

and it will be convenient to identify these two body forces as

$$\mathbf{f}_{12} = \int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \rho_1\,\mathbf{b}_{12}\,dV\,, \quad \mathbf{f}_{21} = \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \rho_2\,\mathbf{b}_{21}\,dV \tag{40}$$

At this point we repeat Eq. (35) as

$$\text{Euler Result I:} \qquad \frac{d}{dt}\big(m\,\mathbf{v}_{\mathrm{CM}}\big) = \mathbf{f} \tag{41}$$

and note that Eqs. (39) and (40) lead to

$$\text{Euler Result II:} \qquad \mathbf{f}_{12} = -\,\mathbf{f}_{21} \tag{42}$$

Equation (41) provides Newton's second law for the cloud of mass points illustrated in Fig. 3, and when applied to a mass point it yields Newton's second law as given by Eq. (2). Equation (42), which was derived by applying Euler's first law to the process illustrated in Fig. 4, is identical to Newton's third law. Here we see that Euler's first law can be used to obtain *all three of Newton's laws*; however, the inverse is not true, i.e., one cannot use Newton's laws for mass points or for a cloud of mass points in order to obtain Euler's first law. Euler's laws are based on the *Euler cut principle* and the assumption that the material under consideration can be treated as a *continuum*. These constructs are not to be found in Newton's treatment of mechanics (Truesdell, 1968)[3].

Given that Euler's first law contains all that is available in Newton's three laws, one must wonder why physicists do not move forward one century and accept Euler's first law as their axiom for mechanics. The answer would appear to be associated with Euler's second law that we examine in the following paragraphs.

Central forces

In the absence of any surface forces, we can express Euler's second law as

$$\frac{d}{dt}\int\limits_{\mathscr{V}_m(t)} \mathbf{r}\times\rho\,\mathbf{v}\,dV = \int\limits_{\mathscr{V}_m(t)} \mathbf{r}\times\rho\,\mathbf{b}\,dV \tag{43}$$

and for the three Eulerian cuts illustrated in Fig. 4 we have

$$\begin{aligned}\text{Cut I}: \frac{d}{dt}\int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{v}_1\,dV &= \int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{b}_{12}\,dV\\ &\quad + \int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{b}_{13}\,dV\end{aligned} \tag{44}$$

$$\begin{aligned}\text{Cut II}: \frac{d}{dt}\int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{v}_2\,dV &= \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{b}_{21}\,dV\\ &\quad + \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{b}_{23}\,dV\end{aligned} \tag{45}$$

$$\begin{aligned}\text{Cut III}: \ &\frac{d}{dt}\left[\int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{v}_1\,dV + \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{v}_2\,dV\right]\\ &= \int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{b}_{13}\,dV + \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{b}_{23}\,dV\end{aligned} \tag{46}$$

Use of Eqs. (44) and (45) in Eq. (46) leads to a constraint on the body forces given by

$$\int\limits_{\mathscr{V}_{\mathrm{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{b}_{12}\,dV + \int\limits_{\mathscr{V}_{\mathrm{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{b}_{21}\,dV = 0 \tag{47}$$

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[3] See "A Program toward the Rediscovering the Rational Mechanics of the Age of Reason", Chapter 2 in *Essays of the History of Mechanics*, C. Truesdell, Springer-Verlag New York Inc., 1968

The position vectors can be expressed in terms of the position vectors locating the centers of mass according to

$$\mathbf{r}_1 = \left(\mathbf{r}_{\mathrm{CM}}\right)_1 + \tilde{\mathbf{r}}_1 \, , \quad \mathbf{r}_2 = \left(\mathbf{r}_{\mathrm{CM}}\right)_2 + \tilde{\mathbf{r}}_2 \tag{48}$$

and this leads to

$$\begin{aligned} &\left(\mathbf{r}_{\mathrm{CM}}\right)_1 \times \int_{\mathscr{V}_{\mathrm{I}}(t)} \rho_1 \, \mathbf{b}_{12} \, dV + \int_{\mathscr{V}_{\mathrm{I}}(t)} \tilde{\mathbf{r}}_1 \times \rho_1 \, \mathbf{b}_{12} \, dV \\ &+ \left(\mathbf{r}_{\mathrm{CM}}\right)_2 \times \int_{\mathscr{V}_{\mathrm{II}}(t)} \rho_2 \, \mathbf{b}_{21} \, dV + \int_{\mathscr{V}_{\mathrm{II}}(t)} \tilde{\mathbf{r}}_2 \times \rho_2 \, \mathbf{b}_{21} \, dV = 0 \end{aligned} \tag{49}$$

Next we make use of Eqs. (39) and (40) to express this result in the form

$$\begin{aligned} &\left[(\mathbf{r}_{\mathrm{CM}})_1 \; - \; (\mathbf{r}_{\mathrm{CM}})_2\right] \times \mathbf{f}_{12} \\ &+ \left[\int_{\mathscr{V}_{\mathrm{I}}(t)} \tilde{\mathbf{r}}_1 \times \rho_1 \, \mathbf{b}_{12} \, dV + \int_{\mathscr{V}_{\mathrm{II}}(t)} \tilde{\mathbf{r}}_2 \times \rho_2 \, \mathbf{b}_{21} \, dV \right] = 0 \end{aligned} \tag{50}$$

In Appendix B we demonstrate that the last term in this result can be neglected when the following constraint is satisfied:

$$\text{Constraint:} \quad \frac{\mathbf{O}(\tilde{\mathbf{r}}_1) \; + \; \mathbf{O}(\tilde{\mathbf{r}}_2)}{\mathbf{O}\left[\left(\mathbf{r}_{\mathrm{CM}}\right)_1 \; - \; \left(\mathbf{r}_{\mathrm{CM}}\right)_2\right]} \ll 1 \tag{51}$$

Under these circumstances, Euler's second law leads to

$$\left[\left(\mathbf{r}_{\mathrm{CM}}\right)_1 \; - \; \left(\mathbf{r}_{\mathrm{CM}}\right)_2\right] \times \mathbf{f}_{12} = 0 \tag{52}$$

There are three ways in which this result can be satisfied, and we list them as

1. $\left(\mathbf{r}_{\mathrm{CM}}\right)_1 - \left(\mathbf{r}_{\mathrm{CM}}\right)_2 = 0$ (53)
2. $\mathbf{f}_{12} = 0$ (54)
3. $\left(\mathbf{r}_{\mathrm{CM}}\right)_1 - \left(\mathbf{r}_{\mathrm{CM}}\right)_2$ and $\mathbf{f}_{12}$ are parallel (55)

Since the first two possibilities can not be generally true, we conclude that the interaction force between two bodies must be *parallel* to the vector $\left(\mathbf{r}_{\mathrm{CM}}\right)_1 - \left(\mathbf{r}_{\mathrm{CM}}\right)_2$. We express this result as

$$\text{Euler Result III:} \; \mathbf{f}_{12} = \Omega_{12} \left[\left(\mathbf{r}_{\mathrm{CM}}\right)_1 - \left(\mathbf{r}_{\mathrm{CM}}\right)_2\right] \tag{56}$$

in which Ω_{12} is some *scalar parameter* of the interaction force law. Equation (56) indicates that the interaction force between two bodies subject to the constraint given by Eq. (51) must act along the line of centers, i.e., it is a *central force*.

In this analysis we have shown that Euler's *first law* contains Newton's *three laws*, while Euler's *second law* provides what is known as the *central force law* for the case of mass-point mechanics. Given the power and economy of Euler's laws, one can wonder why Newton's *three laws* are not discarded in favor of Euler's *two laws*. The answer lies in the fact that the *central force law*, represented by Eq. (56), is a *non-relativistic* phenomenon. Since forces are propagated at the speed of light, the force that one body exerts on another *cannot lie along the line of centers* when the relative velocity between the two bodies approaches the speed of light. Because of this, physicists prefer to view mechanical phenomena in terms of Newton's laws and make use of the central force law as a *special case* which can be discarded when relativistic phenomena are encountered. Engineers, on the other hand, are rarely involved in relativistic phenomena and what is a *special case* for the physicist is the *general case* for the engineer. Because of this, engineers uniformly formulate their mechanical problems in terms of Euler's two laws and the Euler cut principle.

1.4 Euler's laws and Cauchy's equations

At this point we have traveled part of the route that takes us across the interface between Newton's laws of motion and the macroscopic momentum balance. To complete our journey and connect physics and chemical engineering (in the mechanical sense) we need to show how Euler's laws can be used to derive the macroscopic momentum balance given by Eq. (17).

In order to derive the macroscopic momentum balance on the basis of Euler's laws, we must first deal with the stress vector that appears in Eqs. (27) and (28). This leads us to the work of Cauchy (1789-1857). Cauchy's *lemma* indicates that the stress vector acting on one side of a surface is equal and opposite to the stress vector on the other side of the surface leading to (see Appendix C)

$$\text{Cauchy's lemma:} \quad \mathbf{t}_{(\mathbf{n})} = -\,\mathbf{t}_{(-\mathbf{n})} \tag{57}$$

This represents the first step in the development of Cauchy's *fundamental theorem* given by (see Appendix D)

Cauchy's fundamental theorem:

$$\mathbf{t}_{(\mathbf{n})} = \mathbf{n} \cdot \mathbf{T} \tag{58}$$

in which the stress tensor, $\mathbf{T}$, is defined by

$$\mathbf{T} = \left(\mathbf{i}\,\mathbf{t}_{(\mathbf{i})}\right) + \left(\mathbf{j}\,\mathbf{t}_{(\mathbf{j})}\right) + \left(\mathbf{k}\,\mathbf{t}_{(\mathbf{k})}\right) \tag{59}$$

Here we encounter *dyadic multiplication* of vectors which is different from the more well known "dot" product or "cross" product between two vectors. When this result is used in Eq. (27) we obtain

$$\text{Euler I:} \; \frac{d}{dt} \int_{\mathscr{V}_m(t)} \rho \, \mathbf{v} \, dV = \int_{\mathscr{V}_m(t)} \rho \, \mathbf{b} \, dV + \int_{\mathscr{A}_m(t)} \mathbf{n} \cdot \mathbf{T} \, dA \tag{60}$$

and application of the appropriate form of the divergence theorem leads to

$$\text{Euler I:} \; \frac{d}{dt} \int_{\mathscr{V}_m(t)} \rho \, \mathbf{v} \, dV = \int_{\mathscr{V}_m(t)} \rho \, \mathbf{b} \, dV + \int_{\mathscr{V}_m(t)} \nabla \cdot \mathbf{T} \, dV \tag{61}$$

In order to extract a governing differential equation from this result, we need to make use of the Reynolds transport theorem to express the left hand side of Eq. (61) as

$$\frac{d}{dt} \int_{\mathscr{V}_m(t)} \rho \, \mathbf{v} \, dV = \int_{\mathscr{V}_m(t)} \frac{\partial}{\partial t}\left(\rho \mathbf{v}\right) dV + \int_{\mathscr{A}_m(t)} \rho \mathbf{v}\mathbf{v} \cdot \mathbf{n} \, dA \tag{62}$$

While Osborne Reynolds (1842-1912) is often credited with the development of this theorem for interchanging differentiation and integration, Truesdell (1954, page 53) suggests that "the transport theorem is really an alternative formulation

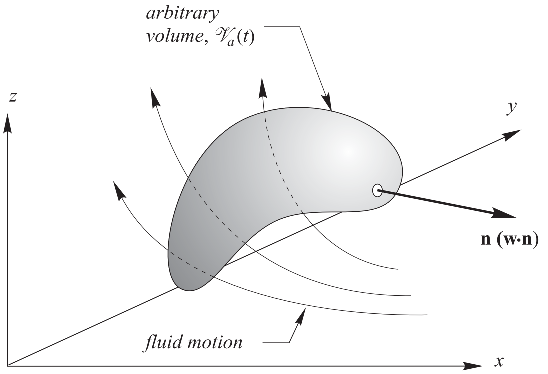


Fig. 5. Arbitrary, moving control volume

of Euler's expansion formula." From a different perspective, one can argue that Eq. (62) is nothing more than a three-dimensional version of the Leibniz (1646-1716) rule for differentiating an integral.

The use of Eq. (62) with Eq. (61) leads to the following form of Euler's first law

$$\int_{\mathscr{V}_m(t)} \frac{\partial}{\partial t}(\rho \mathbf{v})\,dV + \int_{\mathscr{A}_m(t)} \rho \mathbf{v}\mathbf{v}\cdot\mathbf{n}\,dA = \int_{\mathscr{V}_m(t)} \left(\rho\mathbf{b} + \nabla\cdot\mathbf{T}\right)dV \tag{63}$$

and the use of the divergence theorem with the second term provides

$$\int_{\mathscr{V}_m(t)} \left[\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla\cdot(\rho\mathbf{v}\mathbf{v}) - \rho\mathbf{b} - \nabla\cdot\mathbf{T}\right]dV = 0 \tag{64}$$

If we assume that the integrand is continuous and note that the limits of integration are arbitrary, we conclude that the integrand is zero. This leads to what is sometimes referred to as Cauchy's first equation (Truesdell, 1968, page 186).

Cauchy I: $$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla\cdot(\rho\mathbf{v}\mathbf{v}) = \rho\mathbf{b} + \nabla\cdot\mathbf{T} \tag{65}$$

Cauchy's second equation is based on Euler's second law given by Eq. (28) and Cauchy's fundamental theorem given by Eq. (58). The development is complex; however, the final result is quite simple and is given by

Cauchy II: $$\mathbf{T} = \mathbf{T}^{\mathrm{T}} \tag{66}$$

in which $\mathbf{T}^{\mathrm{T}}$ represents the *transpose* of $\mathbf{T}$. In terms of the components of the stress tensor, Eq. (66) takes the form

$$T_{ij} = T_{ji}\,, \quad i,j = 1,2,3 \tag{67}$$

In addition to Cauchy's two equations that one can derive from Euler's two laws of mechanics, we need to add the continuity equation that can be derived from Eq. (29). Use of the Reynolds transport theorem with Eq. (29) provides

Mass:

$$\frac{d}{dt}\int_{\mathscr{V}_m(t)} \rho\,dV = \int_{\mathscr{V}_m(t)} \frac{\partial\rho}{\partial t}dV + \int_{\mathscr{A}_m(t)} \rho\mathbf{v}\cdot\mathbf{n}\,dA = 0 \tag{68}$$

Application of the divergence theorem leads to

$$\int_{\mathscr{V}_m(t)} \left[\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\mathbf{v})\right]dV = 0 \tag{69}$$

and from this we extract the well known continuity equation given by

Continuity equation:

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\mathbf{v}) = 0 \tag{70}$$

Often the continuity equation is used to modify the left hand side of Eq. (65) to obtain

$$\rho\frac{\partial\mathbf{v}}{\partial t} + \rho\mathbf{v}\cdot\nabla\mathbf{v} = \rho\mathbf{b} + \nabla\cdot\mathbf{T} \tag{71}$$

and the *material derivative* can be used to produce the more compact form given by

$$\rho\frac{D\mathbf{v}}{Dt} = \rho\mathbf{b} + \nabla\cdot\mathbf{T} \tag{72}$$

When applying this result to fluids, one often follows the work of Stokes (1819-1903) in which the stress tensor is decomposed according to (Aris, 1962, page 106)

$$\mathbf{T} = -p\,\mathbf{I} + \boldsymbol{\tau} \tag{73}$$

This leads to the viscous stress equations of motion

$$\rho\frac{D\mathbf{v}}{Dt} = \rho\mathbf{b} - \nabla p + \nabla\cdot\boldsymbol{\tau} \tag{74}$$

For linear, isotropic fluids the viscous stress tensor takes the form

$$\boldsymbol{\tau} = \mu\left(\nabla\mathbf{v} + \nabla\mathbf{v}^{\mathrm{T}}\right) + \left(\kappa - \tfrac{2}{3}\mu\right)\nabla\cdot\mathbf{v} \tag{75}$$

in which μ is the shear coefficient of viscosity and κ is the bulk coefficient of viscosity. When compressible viscous effects can be ignored, and the shear coefficient of viscosity can be treated as a constant, substitution of Eq. (75) into Eq. (74) leads to the well known Navier-Stokes equations.

$$\rho\frac{D\mathbf{v}}{Dt} = \rho\mathbf{b} - \nabla p + \mu\nabla^2\mathbf{v} \tag{76}$$

Given Eqs. (65), (66) and (70) we are ready to complete the transition from Newton's laws to the macroscopic momentum balance indicated by Eq. (17).

1.5 Macroscopic momentum balance

In order to develop a completely general macroscopic form of Eq. (65), we make use of an arbitrary moving control volume designated by $\mathscr{V}_a(t)$ in which the "*a*" stands for *arbitrary*. In Fig. 5 we have illustrated an arbitrary moving control volume for which the *speed of displacement* of the control surface is $\mathbf{w}\cdot\mathbf{n}$. The general form of the macroscopic momentum balance is derived by integrating Eq. (65) over $\mathscr{V}_a(t)$ to obtain

$$\int_{\mathscr{V}_a(t)} \left[\frac{\partial}{\partial t}(\rho\mathbf{v}) + \nabla\cdot(\rho\mathbf{v}\mathbf{v})\right]dV = \int_{\mathscr{V}_a(t)} \rho\mathbf{b}\,dV + \int_{\mathscr{V}_a(t)} \nabla\cdot\mathbf{T}\,dV \tag{77}$$

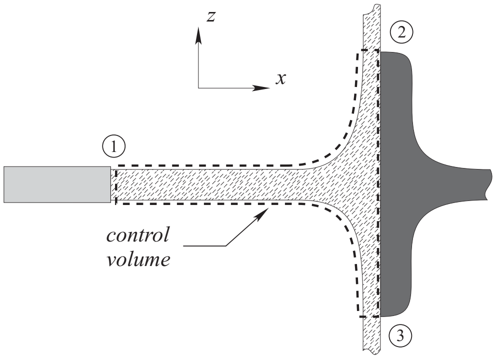


Fig. 6. Control volume for the analysis of the plane jet.

While this result indeed represents the macroscopic momentum balance, only the body force term is *susceptible to macroscopic interpretation*. In order to transform the other terms so that they are also susceptible to macroscopic interpretation, we first use the divergence theorem to transform the volume integrals of $\nabla\cdot(\rho\mathbf{vv})$ and $\nabla\cdot\mathbf{T}$ to area integrals leading to

$$\int_{\mathscr{V}_a(t)} \frac{\partial}{\partial t}(\rho\mathbf{v})\,dV + \int_{\mathscr{A}_a(t)} \rho\mathbf{vv}\cdot\mathbf{n}\,dA = \int_{\mathscr{V}_a(t)} \rho\mathbf{b}\,dV + \int_{\mathscr{A}_a(t)} \mathbf{t}_{(\mathbf{n})}\,dA \tag{78}$$

Here one can see that the first term is certainly not susceptible to macroscopic interpretation; however, use of the general transport theorem (Whitaker, 1981, page 88) provides

$$\frac{d}{dt}\int_{\mathscr{V}_a(t)} \rho\mathbf{v}\,dV = \int_{\mathscr{V}_a(t)} \frac{\partial}{\partial t}(\rho\mathbf{v})\,dV + \int_{\mathscr{A}_a(t)} \rho\mathbf{vw}\cdot\mathbf{n}\,dA \tag{79}$$

When this is used with Eq. (78) we obtain the macroscopic momentum balance in the form

$$\underbrace{\frac{d}{dt}\int_{\mathscr{V}_a(t)} \rho\mathbf{v}\,dV}_{\substack{\text{time rate of change}\\ \text{of momentum in the}\\ \text{control volume}}} + \underbrace{\int_{\mathscr{A}_a(t)} \rho\mathbf{v}(\mathbf{v}-\mathbf{w})\cdot\mathbf{n}\,dA}_{\substack{\text{net flux of momentum}\\ \text{leaving the control volume}}} = \underbrace{\int_{\mathscr{V}_a(t)} \rho\mathbf{b}\,dV}_{\substack{\text{body force acting on the}\\ \text{material in the control volume}}} + \underbrace{\int_{\mathscr{A}_a(t)} \mathbf{t}_{(\mathbf{n})}\,dA}_{\substack{\text{surface force acting on the}\\ \text{material in the control volume}}} \tag{80}$$

This is a precise representation of the result suggested earlier by Eq. (17), and it is only useful for solving macroscopic problems when the terms are *susceptible to macroscopic interpretation*. One classic example of a process that can be analyzed successfully using Eq. (80) is illustrated in Fig. 6. In this case, the *x*-component of the force exerted on the plate can be obtained from Eq. (80) on the basis of a few judicious assumptions. However, it is difficult to create confidence in students by imposing assumptions about kinematics and stress (Euler & Cauchy) when the students have little or no knowledge of these concepts. In many cases, macroscopic balance analysis of flow problems requires the use of the macroscopic mechanical energy equation. This can only be derived starting from Eq. (65), and one is again faced with the necessity of following the path identified by Euler and Cauchy.

1.6 Summary

In the previous paragraphs we have outlined a connection between Newton's laws and Euler's laws as they apply to both mass points and continuous media. Students who travel this path can appreciate the similarities between these two points of view and they can appreciate the differences. They can derive the macroscopic momentum balance and, with practice, they can apply it with confidence. In addition, they can derive and apply tools such as Bernoulli's equation and the mechanical energy equation (Whitaker, 1981, page 221). A quick survey of Eqs. (18) through (80) indicates that a rigorous derivation of the macroscopic momentum balance is not an easy task, and one can certainly question whether the rigorous approach is worth the effort. The answer is YES for two reasons. First, if Eq. (80) is presented as a *recipe* for solving problems, students will only use it with confidence to solve problems that have already been solved. Second, chemical engineering students must deal with multi-component systems in which one is confronted with the *species velocity* and the *species body* (Truesdell, 1969, Lecture 5). Working with these quantities is difficult if one does not have some experience with the developments of Euler and Cauchy.

2. Multicomponent systems

In this section we provide a brief outline of the axioms for the mass and momentum of multicomponent systems, and we present several important forms of the proved theorems associated with these axioms. A key concept associated with the continuum approach to multicomponent transport phenomena is the *species body*. In Fig. 7 we have illustrated a two-component system containing species *A* and species *B* from which we have *cut out* a species *A* body. At $t = 0$ the space occupied by the species *A* body is also occupied by a species *B* body having the same configuration. However, as time evolves the two species separate since their velocities are not equal.

For *single component* transport phenomena, one considers a continuum whose motion is described by

$$\mathbf{r} = \mathbf{r}(\mathbf{R}, t) \tag{81}$$

in which $\mathbf{r}$ represents the time-dependent position of a *material element* whose reference position is $\mathbf{R}$. The velocity of any material element can be expressed as

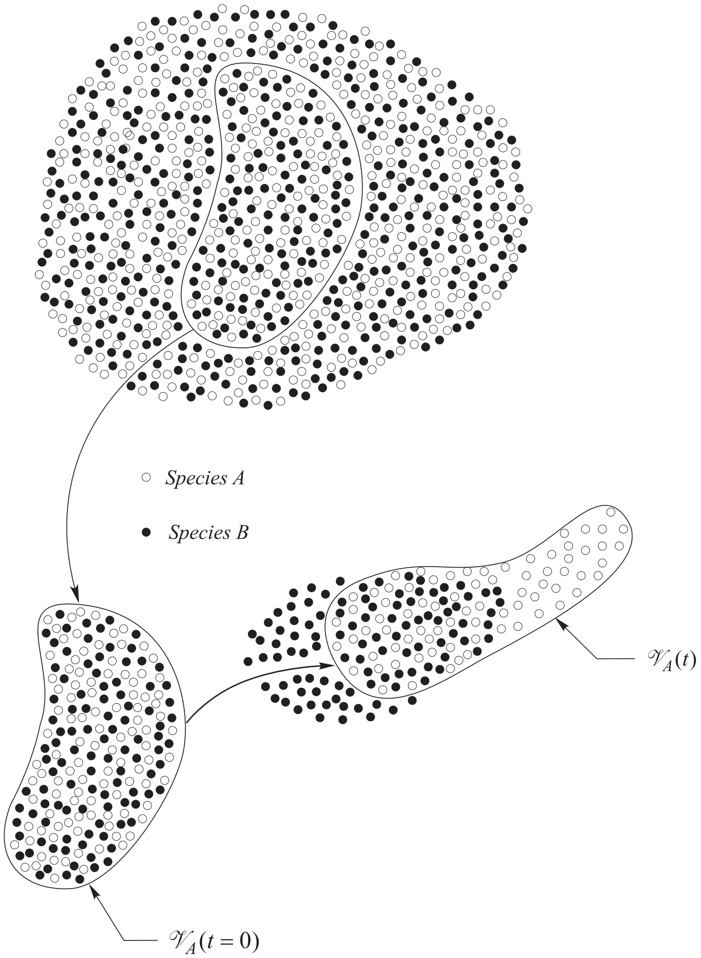


Fig. 7. Motion of a species A body.

$$\mathbf{v} = \left(\frac{d\mathbf{r}}{dt}\right)_{\mathbf{R}} = \frac{D\mathbf{r}}{Dt} \tag{82}$$

in which $D\mathbf{r}/Dt$ is the *material derivative* that appears in Eq. (72). The motion of a species body is described in an analogous manner, thus the motion of a material element of species *A* is represented as

$$\mathbf{r}_A = \mathbf{r}_A(\mathbf{R}_A, t) \tag{83}$$

and the velocity is given by

$$\mathbf{v}_A = \left(\frac{d\mathbf{r}_A}{dt}\right)_{\mathbf{R}_A} \tag{84}$$

Points within the species *A* body illustrated in Fig. 7 move with the velocity, $\mathbf{v}_A$.

2.1 Conservation of mass

In terms of the concept of a species body, we state the two axioms for the mass of multicomponent systems as

Axiom I:

$$\frac{d}{dt}\int_{\mathscr{V}_A(t)} \rho_A \, dV = \int_{\mathscr{V}_A(t)} r_A \, dV \, , \; A = 1, 2, ..., N \tag{85}$$

Axiom II:

$$\sum_{A=1}^{A=N} r_A = 0 \tag{86}$$

Here ρ_A represents the mass density of species *A* while r_A represents the net mass rate of production (per unit volume) of species *A* owing to chemical reaction. In order to extract a governing differential equation from Eq. (85), we make use of the Reynolds transport theorem for the volume $\mathscr{V}_A(t)$ to obtain

$$\frac{d}{dt}\int_{\mathscr{V}_A(t)} \rho_A \, dV = \int_{\mathscr{V}_A(t)} \frac{\partial \rho_A}{\partial t} dV + \int_{\mathscr{A}_A(t)} \rho_A \mathbf{v}_A \cdot \mathbf{n} \, dA \tag{87}$$

and then apply the divergence theorem so that Eq. (85) can be expressed as

$$\int_{\mathscr{V}_A(t)} \left[\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A) - r_A\right] dV = 0 \, , \qquad A = 1, 2, ..., N \tag{88}$$

Here we note that the volume $\mathscr{V}_A(t)$ is arbitrary in the sense that the *Euler cut principle* suggests that we can identify any region in space as the species body. If we assume that the integrand in Eq. (88) is continuous, the arbitrary nature of $\mathscr{V}_A(t)$ leads us to conclude that the integrand must be zero. Requiring that Eq. (88) be satisfied leads to the *species continuity equation* and we repeat the constraint on the reaction rates so that our point equations are given by (Truesdell and Toupin, 1960, Sec. 159)

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A) = r_A , A = 1, 2, ..., N \qquad (89)$$

$$\sum_{A=1}^{A=N} r_A = 0 \qquad (90)$$

It is important to demonstrate how Eqs. (89) and (90) are related to earlier studies of single component transport phenomena and the continuity equation. If we sum Eq. (89) over all species and impose the axiom given by Eq. (90) we obtain

$$\frac{\partial}{\partial t} \sum_{A=1}^{A=N} \rho_A + \nabla \cdot \sum_{A=1}^{A=N} \rho_A \mathbf{v}_A = 0 \qquad (91)$$

We define the *total mass density* as

$$\rho = \sum_{A=1}^{A=N} \rho_A \qquad (92)$$

and note that the mass fraction is given by

$$\omega_A = \rho_A / \rho \qquad (93)$$

In terms of the total mass density Eq. (91) takes the form

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \sum_{A=1}^{A=N} \rho_A \mathbf{v}_A = 0 \qquad (94)$$

and use of the definition of the mass average velocity

$$\mathbf{v} = \sum_{A=1}^{A=N} \omega_A \mathbf{v}_A \text{ , \textit{mass average velocity}} \qquad (95)$$

leads us to

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \qquad (96)$$

This result has exactly the same form as the continuity equation for single component systems; however, one should think of it as having *greater physical content* since the density and velocity are related to the associated species quantities by Eqs. (92) and (95).

2.2 Molar forms

Often the molar form of Eq. (89) is preferred because both reaction rates and phase equilibria are expressed in molar quantities. We can divide Eq. (89) by the molecular mass of species *A* and make use of the definitions

$$c_A = \rho_A / M_A , R_A = r_A / M_A \qquad (97)$$

in order to express Eqs. (89) and (90) as

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}_A) = R_A , A = 1, 2, ..., N \qquad (98)$$

$$\sum_{A=1}^{A=N} M_A R_A = 0 \qquad (99)$$

While Eq. (90) will be of some use to us in our analysis of both the mass and mechanics of multicomponent systems, Eq. (99) will be of very little use. In actual fact, the axiomatic form given by Eq. (86) is less predominate among chemical engineers and chemists than the following statement

$$\left\{ \begin{array}{c} \textit{atomic species are} \\ \textit{neither created nor} \\ \textit{destroyed by chemical} \\ \textit{reactions} \end{array} \right\} \qquad (100)$$

and we need to represent this concept in precise mathematical form.

2.3 Stoichiometry

To be precise about the role of atomic species in chemical reactions, we need to replace the *word statement* given by Eq. (100) with a *word equation* which we write as

$$\left\{ \begin{array}{c} \textit{total molar rate of production} \\ \textit{of J - type atoms owing to} \\ \textit{chemical reactions} \end{array} \right\} = 0 , J = 1, 2, ..., T \qquad (101)$$

From this we need to extract a mathematical equation and in order to do this we define the number N_{JA} as (Amundson, 1966, page 51)

$$N_{JA} = \left\{ \begin{array}{c} \textit{number of J - type} \\ \textit{atoms associated with} \\ \textit{molecular species A} \end{array} \right\} , \begin{array}{l} J = 1, 2, ..., T \\ A = 1, 2, ..., N \end{array} \qquad (102)$$

We will refer to N_{JA} as the *chemical composition indicator*, and we can use this *definition* to express the *axiom* represented by Eq. (101) as

$$\text{Axiom II:} \quad \sum_{A=1}^{A=N} N_{JA} R_A = 0, \; J = 1, 2, ..., T \qquad (103)$$

This represents a precise mathematical statement that atomic species are neither created nor destroyed by chemical reactions, and one can use this result to prove Eq. (86) as a theorem. While the concept expressed by Eq. (100) appears to be quite simple, the application of Eq. (103) requires some thought and the details of the application are given by Cerro *et al.*, (2009).

2.4 Laws of mechanics

It should be clear that Eqs. (98) and (103) are essential elements of chemical engineering, since they have direct application to the design of separation processes and chemical reactors. Use of Eq. (98) requires a knowledge of the *species velocity* which, in turn, requires an understanding of the mechanics of the species body illustrated in Fig. 7. Our approach to the laws of mechanics for multicomponent systems follows the original work of Euler and Cauchy and is based on the perspective of Truesdell (1969, Lecture 5). We begin with the species *A* body illustrated in Fig. 7 and express the balance of species *A* momentum as

$$\text{Axiom I}: \frac{d}{dt}\int_{\mathscr{V}_A(t)} \rho_A \mathbf{v}_A\, dV = \int_{\mathscr{V}_A(t)} \rho_A\, \mathbf{b}_A\, dV + \int_{\mathscr{A}_A(t)} \mathbf{t}_{A(\mathbf{n})}\, dA$$
$$+ \int_{\mathscr{V}_A(t)} \sum_{B=1}^{B=N} \mathbf{P}_{AB}\, dV + \int_{\mathscr{V}_A(t)} r_A \mathbf{v}_A\, dV, A = 1, 2, ..., N \tag{104}$$

The left hand side of this expression represents the time rate of change of linear momentum of the species *A* body and this is analogous to the left hand side of Eq. (27). The first term on the right hand side represents the *body force* acting on the species *A* body. In many cases, the only body force is the gravitational force and $\mathbf{b}_A$ can be replaced by $\mathbf{g}$. The second term on the right hand side represents the *surface force* acting on the surface of the species *A* body. The body force and the surface force are the only forces that appear in Euler's first law, and it is consistent with the work of Euler to refer to $\mathbf{t}_{A(\mathbf{n})}$ as the species *A* stress vector. Because other species may occupy the space identified as $\mathscr{V}_A(t)$, we need to consider the forces that these other species exert on species *A*. We use $\mathbf{P}_{AB}$ to represent the *force per unit volume* that species *B* exerts on species *A*, and this gives rise to the third term on the right hand side of Eq. (104). We will refer to $\mathbf{P}_{AB}$ as a *diffusive force* since it should depend on the *relative velocity* between species *A* and species *B*. This relative velocity is illustrated by the motion depicted in Fig. 7 where species *A* and species *B* obviously have different velocities.

Finally we need to consider the fact that the momentum of the species *A* body may be increased or decreased by the change in the mass of species *A* *owing to chemical reactions*. We represent the source (±) of species *A* momentum per unit volume as $r_A\mathbf{v}_A$ and this leads to the last term on the right hand side of Eq. (104). If species *A* is *consumed* by a chemical reaction, it seems reasonable that the loss of momentum per unit volume would be given by $r_A\mathbf{v}_A$; however, if species *A* is *produced* by the decomposition of species *B*, the gain in momentum per unit volume should be represented by $r_A\mathbf{v}_B$. A precise description of the source of species *A* momentum depends on the details of the chemical reaction process; however, the difference between $\mathbf{v}_A$ and $\mathbf{v}_B$ is on the order of the *diffusion velocity*, and in subsequent paragraphs we will show that this difference is, in general, unimportant in terms of the contribution of $r_A\mathbf{v}_A$ to the species momentum equation.

At this point one can repeat the development of Cauchy's lemma and Cauchy's fundamental theorem using Eq. (104) in order to express the species *A* stress vector as

$$\mathbf{t}_{A(\mathbf{n})} = \mathbf{n}\cdot\mathbf{T}_A \tag{105}$$

Use of this result in Eq. (104) and applying the divergence theorem leads to

$$\frac{d}{dt}\int_{\mathscr{V}_A(t)} \rho_A \mathbf{v}_A\, dV = \int_{\mathscr{V}_A(t)} \rho_A\, \mathbf{b}_A\, dV + \int_{\mathscr{V}_A(t)} \nabla\cdot\mathbf{T}_A\, dV$$
$$+ \int_{\mathscr{V}_A(t)} \sum_{B=1}^{B=N} \mathbf{P}_{AB}\, dV + \int_{\mathscr{V}_A(t)} r_A \mathbf{v}_A\, dV \tag{106}$$

With an appropriate interpretation of the nomenclature, one finds that this result is identical to the second of Eqs. 5.10 of Truesdell (1969, page 85) provided that one interprets Truesdell's *growth of linear momentum* as the last two terms in Eq. (106). Truesdell and Toupin (1960, page 567) refer to $\mathbf{T}_A$ as the *partial stress* while Truesdell (1969, page 82) favors the word *peculiar*.

A variation of the Reynolds transport theorem illustrated by Eq. (87) can be applied to express the first term in Eq. (106) as

$$\frac{d}{dt}\int_{\mathscr{V}_A(t)} \rho_A \mathbf{v}_A\, dV = \int_{\mathscr{V}_A(t)} \frac{\partial}{\partial t}\left(\rho_A \mathbf{v}_A\right) dV + \int_{\mathscr{A}_A(t)} \rho_A \mathbf{v}_A \mathbf{v}_A\cdot\mathbf{n}\, dA \tag{107}$$

Use of this result, along with the divergence theorem, allows us to collect all the terms in Eq. (106) under a single integral over $\mathscr{V}_A(t)$, and from that integral equation we can extract the following point equation for the momentum of species *A*:

$$\underbrace{\frac{\partial}{\partial t}\left(\rho_A \mathbf{v}_A\right)}_{\text{local acceleration}} + \underbrace{\nabla\cdot\left(\rho_A \mathbf{v}_A \mathbf{v}_A\right)}_{\substack{\text{convective}\\ \text{acceleration}}} = \underbrace{\rho_A \mathbf{b}_A}_{\text{body force}} + \underbrace{\nabla\cdot\mathbf{T}_A}_{\substack{\text{surface}\\ \text{force}}}$$
$$+ \underbrace{\sum_{B=1}^{B=N} \mathbf{P}_{AB}}_{\substack{\text{diffusive}\\ \text{force}}} + \underbrace{r_A \mathbf{v}_A}_{\substack{\text{source of momentum}\\ \text{owing to reaction}}} , A = 1, 2, ..., N \tag{108}$$

An appropriate interpretation of the nomenclature used here will indicate that this result is identical to Eq. A2 of Curtiss and Bird (1996) for the case in which $r_A = 0$ provided that one takes into account the different sign convention for the stress.

The second axiom for the species body illustrated in Fig. 7 is the angular momentum equation given by

$$\text{Axiom II}: \frac{d}{dt}\int_{\mathscr{V}_A(t)} \mathbf{r}\times\rho_A \mathbf{v}_A dV = \int_{\mathscr{V}_A(t)} \mathbf{r}\times\rho_A \mathbf{b}_A dV$$
$$+ \int_{\mathscr{A}_A(t)} \mathbf{r}\times\mathbf{t}_{A(\mathbf{n})}\, dA + \int_{\mathscr{V}_A(t)} \sum_{B=1}^{B=N} \mathbf{r}\times\mathbf{P}_{AB}\, dV \tag{109}$$
$$+ \int_{\mathscr{V}_A(t)} \mathbf{r}\times r_A \mathbf{v}_A\, dV, A = 1, 2, ..., N$$

This result is based on the idea that all torques are the moments of forces and all angular momentum results from the moment of linear momentum, a concept in keeping with the perspective of Euler as indicated by Eqs. (27) and (28). Truesdell (1969, page 84) presents a more general version of Axiom II in which a *growth of rotational momentum* is included. The analysis of Eq. (109) is rather long; however, the final result is simply the symmetry of the partial stress tensor as indicated by

$$\mathbf{T}_A \quad = \quad \mathbf{T}_A^{\mathrm{T}}\,, \quad A = 1, 2, ..., N \tag{110}$$

In addition to Axioms I and II, we also impose the following constraint on the *diffusive force*, $\mathbf{P}_{AB}$, that appears in Eq. (104):

Axiom III: $$\sum_{A=1}^{A=N} \sum_{B=1}^{B=N} \mathbf{P}_{AB} = 0 \tag{111}$$

This constraint is required in order that Cauchy's first equation (see Eq. 65) be valid for mixtures. A little thought will indicate that Axiom III is easily satisfied by the condition $\mathbf{P}_{AB} = -\mathbf{P}_{BA}$ which is reminiscent of Newton's third law of *action and reaction* for mass points. However, a law for mass points does not necessarily carry over to a law for continua, thus Eq. (111) represents an appropriate constraint on the diffusive forces.

Hirschfelder *et al.* (1954, page 497) point out that "even in a collision which produces a chemical reaction, mass, momentum and energy are conserved" and the continuum version of this idea is given by:

Axiom IV: $$\sum_{A=1}^{A=N} r_A \mathbf{v}_A = 0 \tag{112}$$

Once again we should note that $r_A \mathbf{v}_A$ may not be a precise representation of the momentum source (±) during a chemical reaction; however, the error will only be on the order of r_A times the diffusion velocity.

2.5 Total momentum equation

In order to compare the results given by Eqs. (108) and (110) with Cauchy's equations, we first sum Eq. (108) over all N species in order to develop the total momentum equation. This is given by

$$\begin{aligned} \frac{\partial}{\partial t} \sum_{A=1}^{A=N} \left(\rho_A \mathbf{v}_A\right) + \nabla \cdot \sum_{A=1}^{A=N} \left(\rho_A \mathbf{v}_A \mathbf{v}_A\right) \\ = \sum_{A=1}^{A=N} \rho_A \mathbf{b}_A + \nabla \cdot \sum_{A=1}^{A=N} \mathbf{T}_A \end{aligned} \tag{113}$$

in which Axioms III and IV have been used to eliminate the sum of the last two terms in Eq. (108). At this point we define the following total or mass average quantities according to

$$\rho = \sum_{A=1}^{A=N} \rho_A, \ \textit{total density} \tag{114}$$

$$\omega_A = \rho_A / \rho, \ \textit{mass fraction} \tag{115}$$

$$\mathbf{v} = \sum_{A=1}^{A=N} \omega_A \mathbf{v}_A, \ \textit{mass average velocity} \tag{116}$$

$$\mathbf{b} = \sum_{A=1}^{A=N} \omega_A \mathbf{b}_A, \ \textit{mass average body force} \tag{117}$$

so that Eq. (113) takes the form

$$\frac{\partial}{\partial t}\left(\rho \mathbf{v}\right) + \nabla \cdot \sum_{A=1}^{A=N} \rho_A \mathbf{v}_A \mathbf{v}_A = \rho \mathbf{b} + \nabla \cdot \sum_{A=1}^{A=N} \mathbf{T}_A \tag{118}$$

In order to extract a simplified form of the convective acceleration, we need to introduce the important concept of a *diffusion velocity*. In the chemical engineering literature, one finds references to a molar diffusion velocity and a mass diffusion velocity; however, it is only the latter that plays a role in the mechanics of multicomponent systems. We define the *mass diffusion velocity* according to the decomposition given by

$$\mathbf{v}_A = \mathbf{v} + \mathbf{u}_A\,, A = 1, 2, ..., N \tag{119}$$

and one can easily show that the mass diffusion velocities are constrained by

$$\sum_{A=1}^{A=N} \rho_A \mathbf{u}_A = 0 \tag{120}$$

The representation given by Eq. (119) can be used to express the convective inertial term in Eq. (118) as

$$\sum_{A=1}^{A=N} \rho_A \mathbf{v}_A \mathbf{v}_A = \sum_{A=1}^{A=N} \rho_A \mathbf{v}_A (\mathbf{v} + \mathbf{u}_A) \tag{121}$$

and a little thought will indicate that this result takes the form

$$\sum_{A=1}^{A=N} \rho_A \mathbf{v}_A \mathbf{v}_A = \rho \mathbf{v} \mathbf{v} + \sum_{A=1}^{A=N} \rho_A \mathbf{v}_A \mathbf{u}_A \tag{122}$$

With the aid of Eq. (119) one can express the last term in this representation as

$$\sum_{A=1}^{A=N} \rho_A \mathbf{v}_A \mathbf{u}_A = \sum_{A=1}^{A=N} \rho_A \mathbf{v} \mathbf{u}_A + \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \mathbf{u}_A \tag{123}$$

and the constraint on the mass diffusion velocities given by Eq. (120) leads to the simplification

$$\sum_{A=1}^{A=N} \rho_A \mathbf{v}_A \mathbf{u}_A = \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \mathbf{u}_A \tag{124}$$

Use of this result in Eq. (122) leads to

$$\sum_{A=1}^{A=N} \rho_A \mathbf{v}_A \mathbf{v}_A = \rho \mathbf{v} \mathbf{v} + \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \mathbf{u}_A \tag{125}$$

and this allows us to write Eq. (118) as

$$\begin{aligned} \frac{\partial}{\partial t}\left(\rho \mathbf{v}\right) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) + \nabla \cdot \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \mathbf{u}_A \\ = \rho \mathbf{b} + \nabla \cdot \sum_{\mathbf{A=1}}^{\mathbf{A=N}} \mathbf{T}_A \end{aligned} \tag{126}$$

At this point it is convenient to define a total stress tensor for multicomponent systems as

$$\mathbf{T} = \sum_{A=1}^{A=N} \mathbf{T}_A - \rho_A \mathbf{u}_A \mathbf{u}_A \tag{127}$$

in which the terms represented by $\rho_A \mathbf{u}_A \mathbf{u}_A$ are referred to as the *diffusive stresses*. Use of this result in Eq. (126) leads us back to Cauchy's first equation given by

Cauchy I: $$\frac{\partial}{\partial t}\left(\rho \mathbf{v}\right) + \nabla \cdot \left(\rho \mathbf{v} \mathbf{v}\right) = \rho \mathbf{b} + \nabla \cdot \mathbf{T} \tag{128}$$

It is easy to see that one can use Eq. (110) along with Eq. (127) to produce the symmetry condition given earlier as Cauchy's second equation.

Cauchy II: $$\mathbf{T} = \mathbf{T}^{\mathrm{T}} \tag{129}$$

The result given by Eq. (127) is identical to Eqs. A6 and A7 of Curtiss and Bird (1996); and Eq. 215.1 of Truesdell and Toupin (1960); however, different choices have been made concerning the *words* used to describe $\mathbf{T}_A$ and different choices have been made concerning the *sign convention* for the stress.

2.6 Stefan-Maxwell's equations

The importance of Eq. (108) is based on the fact that we must determine the species velocity $\mathbf{v}_A$ in order to solve Eq. (98) and thus predict the species concentration, c_A. The task of extracting a useful relation for $\mathbf{v}_A$ from Eq. (108) is not as difficult as it might appear, provided that we are willing to make a few reasonable simplifications. We begin our analysis of the species momentum equation by making use of the following representation for the *species stress tensor*

$$\mathbf{T}_A = -p_A \mathbf{I} + \boldsymbol{\tau}_A \,, \quad \textit{viscous fluid} \tag{130}$$

which is the species analogy of Eq. (73). In this case, p_A is the *partial pressure* of species A and τ_A is the viscous stress tensor for species A. Use of Eq. (130) allows us to write Eq. (108) as

$$\frac{\partial}{\partial t}\left(\rho_A \mathbf{v}_A\right) + \nabla\cdot\left(\rho_A \mathbf{v}_A \mathbf{v}_A\right) = \rho_A \mathbf{b}_A - \nabla p_A + \nabla\cdot\boldsymbol{\tau}_A + \sum_{B=1}^{B=N} \mathbf{P}_{AB} + r_A \mathbf{v}_A \tag{131}$$

In addition to the restrictions imposed by Eq. (130), we now limit our analysis to ideal mixtures so that the partial pressure can be written as

$$p_A = x_A\, p, \ \textit{ideal mixture} \tag{132}$$

in which x_A is the mole fraction of species A and p is the total pressure. Use of this representation for the partial pressure allows us to arrange Eq. (131) in the form

$$\frac{\partial}{\partial t}\left(\rho_A \mathbf{v}_A\right) + \nabla\cdot\left(\rho_A \mathbf{v}_A \mathbf{v}_A\right) - \rho_A \mathbf{b}_A + x_A \nabla p - \nabla\cdot\boldsymbol{\tau}_A - r_A \mathbf{v}_A = -p\nabla x_A + \sum_{B=1}^{B=N} \mathbf{P}_{AB} \,, \ A = 1, 2, ..., N \tag{133}$$

Our next step in the analysis of the species momentum equation is the use of Maxwell's representation for the force $\mathbf{P}_{AB}$ which we express as (Chapman and Cowling, 1970, page 109)

$$\mathbf{P}_{AB} = \frac{p x_A x_B (\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}} \,, \ A, B = 1, 2, ..., N \tag{134}$$

It should be intuitively appealing that the force exerted by species B on species A should depend on the velocity difference, $\mathbf{v}_B - \mathbf{v}_A$. In addition, one can develop arguments to show that the term $p x_A x_B$ is proportional to the *frequency of collisions* between A and B, and the force exerted by B on A should certainly be proportional to the frequency of collisions between the two molecular species. It is important to understand that Eq. (134) was developed for dilute gases in which only binary collisions need be considered, and that the details of the collision process are accounted for in the binary diffusion coefficient, $\mathscr{D}_{AB}$. The binary diffusion coefficients all satisfy the relation

$$\mathscr{D}_{AB} = \mathscr{D}_{BA} \,, \quad A, B = 1, 2, ..., N \tag{135}$$

and when we substitute Eq. (134) into Eq. (133) we obtain a result that can be expressed as

$$p^{-1}\left[\frac{\partial}{\partial t}\left(\rho_A \mathbf{v}_A\right) + \nabla\cdot\left(\rho_A \mathbf{v}_A \mathbf{v}_A\right) - \rho_A \mathbf{b}_A + x_A \nabla p - \nabla\cdot\boldsymbol{\tau}_A - r_A \mathbf{v}_A\right] = -\nabla x_A + \sum_{B=1}^{B=N} \frac{x_A x_B (\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}} \,, A = 1, 2, ..., N \tag{136}$$

Here we have N equations for the N species velocity, $\mathbf{v}_A$, $\mathbf{v}_B$, …, $\mathbf{v}_N$, and it would appear that we are faced with an extremely complex problem. Nowhere in the chemical engineering literature is one confronted with this equation as a means for determining the species velocity, and the reason for this is that the N *complex equations* represented by Eqs. (136) can be arranged in terms of N relatively *simple equations*. The reason for this simplicity is that the left hand side of Eqs. (136) is *usually small* compared to the two terms on the right hand side. We can express this situation as

$$\varepsilon_A = \Omega_A + \Psi_A \,, A = 1, 2, 3, ..., N \tag{137a}$$

$$\varepsilon_A \ll \Omega_A \,, \Psi_A \,, \ A = 1, 2, 3, ..., N \tag{137b}$$

however, if we set $\varepsilon_A = 0$ we are left with only $N-1$ independent equations since Ω_A and Ψ_A are constrained by

$$\sum_{A=1}^{A=N} \Omega_A = 0 \,, \sum_{A=1}^{A=N} \Psi_A = 0 \tag{138}$$

To develop the simple equations associated with Eqs. (136), we first note that the sum over all N equations leads to

$$p^{-1}\sum_{A=1}^{A=N}\left[\frac{\partial}{\partial t}\left(\rho_A \mathbf{v}_A\right) + \nabla\cdot\left(\rho_A \mathbf{v}_A \mathbf{v}_A\right) - \rho_A \mathbf{b}_A + x_A \nabla p - \nabla\cdot\boldsymbol{\tau}_A - r_A \mathbf{v}_A\right] = 0 \tag{139}$$

This can be arranged in the form

$$\frac{\partial}{\partial t}\left(\rho \mathbf{v}\right) + \nabla\cdot\left(\rho \mathbf{v}\mathbf{v}\right) = \sum_{A=1}^{A=N} \rho_A \mathbf{b}_A - \nabla p + \nabla\cdot\sum_{A=1}^{A=N}\left(\boldsymbol{\tau}_A - \rho_A \mathbf{u}_A \mathbf{u}_A\right) + \sum_{A=1}^{A=N} r_A \mathbf{v}_A \tag{140}$$

and on the basis of Eqs. (112) and (117) we have

$$\frac{\partial}{\partial t}\left(\rho \mathbf{v}\right) + \nabla\cdot\left(\rho \mathbf{v}\mathbf{v}\right) = \rho \mathbf{b} - \nabla p + \nabla\cdot\sum_{A=1}^{A=N}\left(\boldsymbol{\tau}_A - \rho_A \mathbf{u}_A \mathbf{u}_A\right) \tag{141}$$

It is consistent with the definition of the stress tensor given by Eq. (127) to define the viscous stress tensor according to

$$\boldsymbol{\tau} = \sum_{A=1}^{A=N}\left(\boldsymbol{\tau}_A - \rho_A \mathbf{u}_A \mathbf{u}_A\right) \tag{142}$$

Use of this result along with the continuity equation given by Eq. (70) allows us to express Eq. (141) in the form

$$\rho \frac{D\mathbf{v}}{Dt} = \rho \mathbf{b} - \nabla p + \nabla\cdot\boldsymbol{\tau} \tag{143}$$

Rather than attempt to solve Eqs. (136) for all the N species velocities, we use Eq. 143 to determine the mass average velocity and Eqs. (136) to determine N–1 species velocities. This means that the $N-1$ species velocities are determine by

$$p^{-1}\left[\frac{\partial}{\partial t}\left(\rho_A\mathbf{v}_A\right)+\nabla\cdot\left(\rho_A\mathbf{v}_A\mathbf{v}_A\right)-\rho_A\mathbf{b}_A+x_A\nabla p\right.$$
$$\left.-\nabla\cdot\boldsymbol{\tau}_A-r_A\mathbf{v}_A\right]=-\nabla x_A+\sum_{B=1}^{B=N}\frac{x_Ax_B(\mathbf{v}_B-\mathbf{v}_A)}{\mathscr{D}_{AB}},\quad A=1,2,...,N-1 \tag{144}$$

while the N^{th} species velocity is determined by

$$\mathbf{v}_N=\frac{1}{\omega_N}\left[\mathbf{v}-\left(\omega_A\mathbf{v}_A+\omega_B\mathbf{v}_B+......+\omega_{N-1}\mathbf{v}_{N-1}\right)\right] \tag{145}$$

in which $\mathbf{v}$ is obtained from a solution of Eq. (143).

The use of Eqs. (143) and (144) in place of Eqs. (136) will only be of value if the left hand side of Eqs. (144) is negligible. We assume that this is the case and we assume that *small causes give rise to small effects* (Birkhoff, 1960, page 4) so that Eq. (144) leads to the well known Stefan-Maxwell equations given by

$$0=-\nabla x_A+\sum_{B=1}^{B=N}\frac{x_Ax_B(\mathbf{v}_B-\mathbf{v}_A)}{\mathscr{D}_{AB}},\ A=1,2,...,N-1 \tag{146}$$

If the ideal mixture relation given by Eq. (132) is replaced with a general equation of state

$$p_A=f(x_A,x_B,x_C,....,x_{N-1},T,p) \tag{147}$$

the analysis becomes more complex and the details are presented in Appendix E. There we conclude that the so-called generalized Stefan-Maxwell equations should take the form

$$-x_A\nabla\ln\left(\gamma_A\right)=-\frac{x_A}{RT}\nabla\mu_A$$
$$+\sum_{B=1}^{B=N}\frac{x_Ax_B(\mathbf{v}_B-\mathbf{v}_A)}{\mathscr{D}_{AB}},A=1,2,...,N-1 \tag{148}$$

in which γ_A is the activity coefficient and μ_A is the chemical potential. When Eq. (132) is indeed a valid approximation for the partial pressure, Eq. (146) can be used with confidence provided that the following inequality is satisfied:

$$p^{-1}\left[\frac{\partial}{\partial t}\left(\rho_A\mathbf{v}_A\right)+\nabla\cdot\left(\rho_A\mathbf{v}_A\mathbf{v}_A\right)-\rho_A\mathbf{b}_A\right.$$
$$\left.+x_A\nabla p-\nabla\cdot\boldsymbol{\tau}_A-r_A\mathbf{v}_A\right]\ll\nabla x_A \tag{149}$$
$$\text{or}\quad\sum_{B=1}^{B=N}\frac{x_Ax_B(\mathbf{v}_B-\mathbf{v}_A)}{\mathscr{D}_{AB}},\quad A=1,2,...,N-1$$

Here we have indicated that we can compare the left hand side of Eq. (144) with either of the two terms on the right hand side. In general, it is easier to estimate ∇x_A but there may be situations in which the second term involving $\mathbf{v}_B-\mathbf{v}_A$ is preferred. The *constraints* related with the *restrictions* associated with Eq. (149) were originally explored by Whitaker (1986, page 9); however, more reliable constraints can be developed by using the total momentum equation to simplify the left hand side of Eq. (149), and this is done in the following paragraphs.

In order to simplify the terms on the left hand side of Eq. (149), we represent the species velocity in terms of the mass average velocity and the diffusion velocity

$$\mathbf{v}_A=\mathbf{v}+\mathbf{u}_A \tag{150}$$

to obtain the following expression

$$p^{-1}\left[\frac{\partial}{\partial t}\left(\rho_A\mathbf{v}_A\right)+\nabla\cdot\left(\rho_A\mathbf{v}_A\mathbf{v}_A\right)-\rho_A\mathbf{b}_A\right.$$
$$\left.+x_A\nabla p-\nabla\cdot\boldsymbol{\tau}_A-r_A\mathbf{v}_A\right]$$
$$=p^{-1}\left[\rho_A\left(\frac{\partial\mathbf{v}}{\partial t}+\mathbf{v}\cdot\nabla\mathbf{v}\right)-\rho_A\mathbf{b}_A\right.$$
$$\left.+x_A\nabla p-\nabla\cdot\boldsymbol{\tau}_A\right]$$
$$+p^{-1}\left[\rho_A\left(\frac{\partial\mathbf{u}_A}{\partial t}+\mathbf{v}_A\cdot\nabla\mathbf{u}_A+\mathbf{u}_A\cdot\nabla\mathbf{v}\right)\right] \tag{151}$$

Here we have made repeated use of Eq. (150) along with the continuity equation given by Eq. (89). At this point we can make use of Eq. (74) to simplify Eq. (151) to the form

$$p^{-1}\left[\frac{\partial}{\partial t}\left(\rho_A\mathbf{v}_A\right)+\nabla\cdot\left(\rho_A\mathbf{v}_A\mathbf{v}_A\right)-\rho_A\mathbf{b}_A\right.$$
$$\left.+x_A\nabla p-\nabla\cdot\boldsymbol{\tau}_A-r_A\mathbf{v}_A\right]$$
$$=p^{-1}\rho_A(\mathbf{b}-\mathbf{b}_A)-p^{-1}(\omega_A-x_A)\nabla p \tag{152}$$
$$+p^{-1}\left(\omega_A\nabla\cdot\boldsymbol{\tau}-\nabla\cdot\boldsymbol{\tau}_A\right)$$
$$+p^{-1}\rho_A\left(\frac{\partial\mathbf{u}_A}{\partial t}+\mathbf{v}_A\cdot\nabla\mathbf{u}_A+\mathbf{u}_A\cdot\nabla\mathbf{v}\right)$$

and this allows us to express Eq. (149) as

$$p^{-1}\rho_A(\mathbf{b}-\mathbf{b}_A)-p^{-1}(\omega_A-x_A)\nabla p$$
$$+p^{-1}\left(\omega_A\nabla\cdot\boldsymbol{\tau}-\nabla\cdot\boldsymbol{\tau}_A\right)$$
$$+p^{-1}\rho_A\left(\frac{\partial\mathbf{u}_A}{\partial t}+\mathbf{v}_A\cdot\nabla\mathbf{u}_A+\mathbf{u}_A\cdot\nabla\mathbf{v}\right)\ll\nabla x_A \tag{153}$$
$$\text{or}\quad\sum_{B=1}^{B=N}\frac{x_Ax_B(\mathbf{v}_B-\mathbf{v}_A)}{\mathscr{D}_{AB}},\ A=1,2,...,N-1$$

The various terms on the left hand side of this inequality can take on both positive and negative values, and a conservative approach to satisfying the inequality is to require the following four inequalities

$$p^{-1}\rho_A(\mathbf{b}-\mathbf{b}_A)\ll\nabla x_A\ \text{or}\ \sum_{B=1}^{B=N}\frac{x_Ax_B(\mathbf{v}_B-\mathbf{v}_A)}{\mathscr{D}_{AB}} \tag{154a}$$

$$p^{-1}(\omega_A-x_A)\nabla p\ll\nabla x_A\ \text{or}\ \sum_{B=1}^{B=N}\frac{x_Ax_B(\mathbf{v}_B-\mathbf{v}_A)}{\mathscr{D}_{AB}} \tag{154b}$$

$$p^{-1}\left(\omega_A\nabla\cdot\boldsymbol{\tau}-\nabla\cdot\boldsymbol{\tau}_A\right)\ll\nabla x_A\ \text{or}\ \sum_{B=1}^{B=N}\frac{x_Ax_B(\mathbf{v}_B-\mathbf{v}_A)}{\mathscr{D}_{AB}} \tag{154c}$$

$$p^{-1}\rho_A\left(\frac{\partial\mathbf{u}_A}{\partial t}+\mathbf{v}_A\cdot\nabla\mathbf{u}_A+\mathbf{u}_A\cdot\nabla\mathbf{v}\right)\ll\nabla x_A$$

$$\text{or} \quad \sum_{B=1}^{B=N} \frac{x_A x_B (\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}} \tag{154d}$$

Here it is understood that these inequalities apply to $A = 1, 2, ..., N-1$. We refer to these inequalities as *restrictions* that must be satisfied if the Stefan-Maxwell equations are to provide reliable solutions to the N–1 species momentum equations. In order to obtain *constraints* (Whitaker, 1988) we must develop estimates of all the terms. If gravity is the only body force, we have $\mathbf{b} = \mathbf{b}_A = \mathbf{g}$ and Eq. (154a) is automatically satisfied. However, if species A is an ionic species and an electrostatic field exists, the body force term must be retained and Eq. (146) must be modified in an appropriate manner (Bird *et al.*, 2002, page 781). The restriction given by Eq. (154b) indicates that we need an estimate of ∇p and for some processes this may be difficult. The third restriction given by Eq. (154c) presents a problem since little is known about the partial stress, $\boldsymbol{\tau}_A$, however, it seems plausible that

$$\omega_A \nabla \cdot \boldsymbol{\tau} - \nabla \cdot \boldsymbol{\tau}_A < \omega_A \nabla \cdot \boldsymbol{\tau} \tag{155}$$

which leads to the more conservative restriction given by

$$p^{-1} \left(\omega_A \nabla \cdot \boldsymbol{\tau} \right) \ll \nabla x_A \quad \text{or} \quad \sum_{B=1}^{B=N} \frac{x_A x_B (\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}} \tag{156}$$

In this case one might be able to use Eq. (75) to obtain an estimate of $\nabla \cdot \boldsymbol{\tau}$ and thus develop a *constraint* associated with the *restriction* given by Eq. (154c).

The inequality given by Eq. (154d) involves the diffusion velocity, thus it might be easier to explore this restriction in the form

$$p^{-1} \rho_A \left(\frac{\partial \mathbf{u}_A}{\partial t} + \mathbf{v}_A \cdot \nabla \mathbf{u}_A + \mathbf{u}_A \cdot \nabla \mathbf{v} \right) \ll \sum_{B=1}^{B=N} \frac{x_A x_B (\mathbf{u}_B - \mathbf{u}_A)}{\mathscr{D}_{AB}}, \, A = 1, 2, .., N-1 \tag{157}$$

since both sides of the inequality are directly related to the diffusion velocity. For gas phase processes, it may be convenient to approximate the pressure according to (Whitaker, 1981, page 402)

$$p \sim \rho C^2 \tag{158}$$

where C represents the speed of sound that is on the order of 300m/s for a gas at atmospheric pressure.

The problem of establishing the *domain of validity* of the Stefan-Maxwell equations is much more difficult than identifying the constraints associated with laminar boundary layer theory (Schlichting, 1968, page 117) or lubrication theory (Batchelor, 1967, page 219) or geostrophic flows (Dutton, 1976, page 512). Those special cases are well known and have received considerable attention while the species momentum equation has generally been ignored as a source of information for the solution of mass transfer problems. In the next section we examine the classic diffusion process associated with the Stefan diffusion tube and we illustrate how one could begin to explore the inequalities given by Eqs. (154).

2.7 Stefan diffusion tube

In the previous paragraphs we have outlined an approach to the determination of the species velocity, $\mathbf{v}_A$ where A = 1, 2, …, N. Various approximations have been imposed, such as the ideal mixture condition given by Eq. (132) and the simplified representation for the diffusive force given by Eq. (134). While *restrictions* have been imposed that allow us to derive the Stefan-Maxwell equations, no *constraints* have been presented (Whitaker, 1988). Here one must remember that restrictions indicate *what* must occur in order for a result to be valid, while constraints indicate *when* these conditions occur in terms of parameters that are known *a priori*. To illustrate how one can develop constraints, we consider the classic process of binary diffusion in the Stefan diffusion tube illustrated in Fig. 8. In this example, we assume that the gas passing over the top of the tube is pure species B and that the liquid in the bottom of the tube is pure species A.

For a binary diffusion process, there are *two momentum equations* to be considered. One of these should be a Stefan-Maxwell equation as indicated by Eq. (146) while the other should be the *total momentum equation* as indicated by Eq. (143). However, in the classic analysis of the Stefan diffusion tube (Bird *et al.*, 202, page 545), the *total momentum equation* is ignored and is replaced by the following assumption for the velocity of species B in the gas phase:

$$\text{Assumption:} \qquad \mathbf{v}_B = 0 \tag{159}$$

The motivation for discarding Eq. (143) in favor of Eq. (159) is based on the fact that $\mathbf{v}_B$ is *very small* compared to $\mathbf{v}_A$ and is, in fact, small enough so that it can be set equal to zero. The restriction given by

$$\text{Restriction:} \qquad \mathbf{v}_B \ll \mathbf{v}_A \tag{160}$$

is consistent with Eq. (159) if one is willing to assume that small causes give rise to small effects. One can be more precise about the velocity of species B and note that

$$\mathbf{v}_B = \mathbf{k} \frac{d\ell}{dt}, \; z = \ell(t) \tag{161}$$

if the solubility of species B in species A is negligible. The species jump condition (Whitaker, 1992) can be used to estimate the velocity of species A in the gas phase according to

$$\mathbf{v}_A = \mathbf{O}\left(c_{A,liq} / c_{A,gas} \right) \frac{d\ell}{dt} \tag{162}$$

When this estimate is compared with Eq. (161) we conclude that the assumption given by Eq. (159) can be replaced with the following constraint:

$$\text{Constraint:} \qquad \left(c_{A,liq} / c_{A,gas} \right) \gg 1 \tag{163}$$

While the simplification indicated by Eq. (159) is certainly plausible based on the constraint given by Eq. (163), discarding a *governing equation* should al-

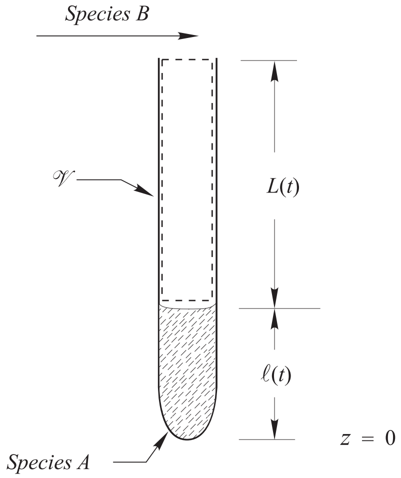


Fig. 8. Stefan diffusion tube.

ways be done with care. Having provided some words of caution, we adopt Eq. (159) as an acceptable solution to the momentum equation for species *B*.

The second momentum equation is the species momentum equation for species *A* and this is given by Eq. (146). For the binary system under consideration, with the constraint indicated by Eq. (159), the species *A* momentum equation takes the form

$$\text{Species } A\text{:} \qquad 0 = -\nabla x_A - \frac{x_A x_B \mathbf{v}_A}{\mathscr{D}_{AB}} \tag{164}$$

Equation (159) could be considered as one of Birkhoff's (1960, page 4) plausible intuitive hypotheses, while Eq. (164) is a result of imposing the restrictions indicated by Eqs. (154).

Body force

To explore the first of the restrictions given by Eqs. (154), we consider a binary system subject to Eq. (159) in order to obtain

$$\text{Restriction:} \quad p^{-1}\rho_A(\mathbf{b} - \mathbf{b}_A) \ll \frac{x_A x_B \mathbf{v}_A}{\mathscr{D}_{AB}} \tag{165}$$

Use of the definition given by Eq. (117) leads to

$$p^{-1}\rho_A\omega_B(\mathbf{b}_B - \mathbf{b}_A) \ll \frac{x_A x_B \mathbf{v}_A}{\mathscr{D}_{AB}} \tag{166}$$

For a binary system with $\mathbf{v}_B = 0$ the velocity of species *A* is related to the mass average velocity by

$$\mathbf{v}_A = \frac{\mathbf{v}}{\omega_A} \tag{167}$$

We can use this result, along with Eq. (158), to express the body force restriction in terms of the following constraint:

$$\text{Constraint:} \ \frac{x_A(1-x_A)}{\omega_A(1-\omega_A)} \frac{M\,C^3}{\mathscr{D}_{AB}} \gg \omega_A \left| \mathbf{b}_B - \mathbf{b}_A \right| \tag{168}$$

in which *M* is the Mach number defined by

$$M = \frac{\mathrm{v}}{C} \tag{169}$$

For a binary system, the constraint given by Eq. (168) will generally be satisfied by the assumption

$$\mathbf{b}_A = \mathbf{b}_B = \mathbf{g} = \mathbf{b} \tag{170}$$

since a ternary system will be required to produce ionic species and body forces that are different than the gravitational force.

Viscous force

At this point we ignore the restriction given by Eq. (154b) and move on to the restriction given by Eq. (154c). This can be used, in the form given by Eq. (156), with Eq. (164) to obtain

$$\text{Restriction:} \quad p^{-1}\,\omega_A\,\nabla\cdot\boldsymbol{\tau} \ll \frac{x_A x_B \mathbf{v}_A}{\mathscr{D}_{AB}} \tag{171}$$

Estimating viscous effects for process illustrated in Fig. 8 is not a straightforward matter. For the classic problem of laminar flow in a tube, one could estimate the viscous stress and its divergence as (Whitaker, 1986, page 16)

$$\boldsymbol{\tau} = \mathbf{O}\big(\mu\,\mathrm{v}/D\big), \quad \nabla\cdot\boldsymbol{\tau} = \mathbf{O}\big(\mu\,\mathrm{v}/D^2\big) \tag{172}$$

Here μ represents the viscosity, **v** represents the mass average velocity, and *D* represents the diameter of the tube as indicated in Fig. 8. This estimate of $\nabla\cdot\boldsymbol{\tau}$ would be appropriate for the parabolic velocity profile shown in Fig. 9a but not for the flat velocity profile (Whitaker, 1967) shown in Fig. 9b. An approach that is more appropriate for the diffusive process illustrated in Fig. 9b is to estimate the value of $\nabla\cdot\boldsymbol{\tau}$ using the average value according to

$$\nabla\cdot\boldsymbol{\tau} \sim \langle\nabla\cdot\boldsymbol{\tau}\rangle = \frac{1}{\mathscr{V}}\int_{\mathscr{V}} \nabla\cdot\boldsymbol{\tau}\,dV = \frac{1}{\mathscr{V}}\int_{\mathscr{A}} \mathbf{n}\cdot\boldsymbol{\tau}\,dA \tag{173}$$

Here $\mathscr{V}$ is the control volume illustrated in Fig. 8 and $\mathscr{A}$ is the surface area of that control volume. In terms of the three distinct areas associated with the control volume, this result takes the from

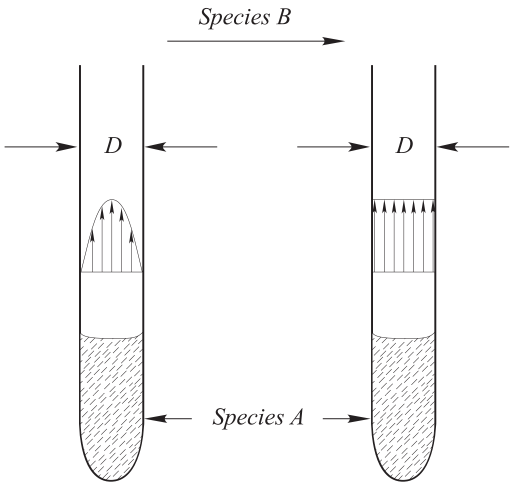
$$\langle\nabla\cdot\boldsymbol{\tau}\rangle = \frac{\langle\tau_{zz}\rangle\big|_{z=L(t)+\ell(t)}}{L(t)} - \frac{\langle\tau_{zz}\rangle\big|_{z=\ell(t)}}{L(t)} + \frac{4}{D}\langle\tau_{rz}\rangle\big|_{r=D/2} \tag{174}$$

It seems plausible to neglect the viscous stresses at the entrance and exit of the control in order to simplify this result to

$$\langle\nabla\cdot\boldsymbol{\tau}\rangle = \frac{4\langle\tau_{rz}\rangle\big|_{r=D/2}}{D} \tag{175}$$

In order to develop an estimate of $\langle\tau_{rz}\rangle$ at the wall, we first make use of Maxwell's one-sided flux expression given by (Kennard, 1938, page 63)

$$\left\{\begin{matrix}\text{flux of species } A \\ \text{crossing a surface} \\ \text{from one side}\end{matrix}\right\} = \tfrac{1}{4}\,n_A\,C_A \tag{176}$$



(a) pressure driven flow (b) diffusion driven flow

Fig. 9. Velocity profiles in a Stefan diffusion tube

Here n_A is the *number density* of species A and C_A is the mean speed of species A which is on the order of the speed of sound. It is important to note that Eq. (176) is valid for an unbounded gas at equilibrium. In our analysis of the momentum transfer process at a gas-solid interface, we *assume* that the rate at which molecules strike the surface is given by

$$\left\{\begin{matrix}\text{flux of species } A \text{ molecules}\\ \text{incident upon a wall bounding}\\ \text{a semi-infinite region}\end{matrix}\right\} = \tfrac{1}{4} n_A\, C_A \tag{177}$$

The idea behind the application of Eq. (176) to produce Eq. (177) is that the molecules leaving the wall do not alter the nature of the incoming molecules.

When the *mean free path is small compared to the tube diameter*, the tangential component of momentum that is transferred to the wall by an *incoming molecule* can be approximated by

$$\left\{\begin{matrix}\text{average tangential component}\\ \text{of momentum transferred to the}\\ \text{wall per molecule of species } A\end{matrix}\right\} = m_A \,\mathrm{v}_{Az}\big|_{r=D/2} \tag{178}$$

in which m_A is the mass of a molecule of species A. Here we have evaluated the momentum of a molecule of species A at the wall because the mean free path for species A is small compared to the tube diameter. To be very clear about this situation, we denote the mean free path of species A by ℓ_A and note that Eq. (178) is constrained by the inequality

$$\ell_A \ll D \tag{179}$$

In order to obtain the *rate* of tangential momentum transferred to the wall by species A, we multiply the flux of species A by the momentum of species A leading to

$$\left\{\begin{matrix}\text{rate of tangential}\\ \text{momentum transferred to}\\ \text{the wall by species } A\end{matrix}\right\} = \frac{1}{4} n_A\, C_A\, m_A \,\mathrm{v}_{Az}\big|_{r=D/2} \tag{180}$$

This representation for the rate of tangential momentum transferred to the wall by species A assumes that there is no net tangential momentum associated with the molecules *reflected* from the wall, i.e., the molecules are *diffusely scattered* by the wall. To obtain the total rate of tangential momentum transferred to the wall, we sum over all species to obtain

$$\left\{\begin{matrix}\text{total rate of tangential}\\ \text{momentum transferred}\\ \text{to the wall}\end{matrix}\right\} = \sum_{A=1}^{A=N} \frac{1}{4} n_A\, C_A\, m_A \,\mathrm{v}_{Az}\big|_{r=D/2} \tag{181}$$

The species density is the mass of a molecular times the number density

$$\rho_A = n_A m_A \,, \quad A = 1, 2, ..., N \tag{182}$$

and use of this result in Eq. (181) leads to

$$\left\{\begin{matrix}\text{total rate of tangential}\\ \text{momentum transferred}\\ \text{to the wall}\end{matrix}\right\} = \sum_{A=1}^{A=N} \frac{1}{4} \rho_A\, C_A \,\mathrm{v}_{Az}\big|_{r=D/2} \tag{183}$$

Here we recognize that the total rate of tangential momentum transferred to the wall is equal to the shear stress at the wall, and we express this idea as

$$\left\{\begin{matrix}\text{total rate of tangential}\\ \text{momentum transferred}\\ \text{to the wall}\end{matrix}\right\} = \langle \tau_{rz} \rangle\big|_{r=D/2} = \sum_{A=1}^{A=N} \frac{1}{4} \rho_A\, C_A \,\mathrm{v}_{Az}\big|_{r=D/2} \tag{184}$$

For the special *binary system* under consideration, we have $\mathrm{v}_{Bz} \ll \mathrm{v}_{Az}$ and the rate of transfer of tangential momentum takes the form

$$\langle \tau_{rz} \rangle\big|_{r=D/2} = \frac{1}{4} \rho_A\, C_A \,\mathrm{v}_{Az}\big|_{r=D/2} \tag{185}$$

Directing our attention to the flat velocity profile illustrated in Fig. 9b, we use this result in Eq. (175) to obtain

$$\nabla \cdot \boldsymbol{\tau} \sim \langle \nabla \cdot \boldsymbol{\tau} \rangle = \frac{\rho_A\, C_A \,\mathrm{v}_{Az}}{D} \tag{186}$$

Use of Eq. (186) in Eq. (171) provides the inequality

$$p^{-1} \frac{\omega_A\, \rho_A\, C_A \,\mathrm{v}_{Az}}{D} \ll \frac{x_A x_B \,\mathrm{v}_{Az}}{\mathscr{D}_{AB}} \tag{187}$$

At this point it is convenient to represent the pressure using Eq. (158) and use the approximation $C_A \approx C$ in order to extract the following constraint from Eq. (187):

$$\text{Constraint:} \qquad \frac{x_A(1-x_A)}{\omega_A^2} \frac{CD}{\mathscr{D}_{AB}} \gg 1 \tag{188}$$

Given the following values for the system illustrated in Fig. 8

$$C \sim 300 \text{ m/s} \,, \ \mathscr{D}_{AB} \sim 0.1 \text{cm}^2/\text{s} \,, \ D \sim 0.1 \text{ cm} \tag{189}$$

we find that

$$\frac{C\,D}{\mathcal{D}_{AB}} \sim 3\times 10^4 \tag{190}$$

and the constraint given by Eq. (188) will generally be satisfied unless x_A is very, very close to one. One could also argue that the constraint given by Eq. (188) could also fail when D is much, much less than 0.1 cm; however, the tube diameter must be much, much larger than the mean free diameter, as indicated by Eq. (179), thus arbitrarily small values of D are excluded from this analysis.

Pressure force

Returning to the restriction given by Eq. (154b), we make use of Eq. (159) to obtain the inequality

$$\text{Restriction:}\quad p^{-1}(\omega_A - x_A)\nabla p \ll \frac{x_A x_B \mathbf{v}_A}{\mathcal{D}_{AB}} \tag{191}$$

In this case we *estimate* the pressure gradient as

$$\nabla p = \mathbf{O}\left(\frac{\langle p\rangle\big|_{z=\ell(t)} \; - \; \langle p\rangle\big|_{z=L(t)+\ell(t)}}{L(t)} \right) \tag{192}$$

To obtain a representation for the pressure change in the tube, we make use of the macroscopic momentum balance associated with Eq. (143) when inertial effects are negligible. This gives rise to a macroscopic momentum balance of the form

$$\begin{aligned} 0 = & -\Big(\langle p\rangle\big|_{z=L(t)+\ell(t)} \; - \; \langle p\rangle\big|_{z=\ell(t)}\Big)\frac{\pi D^2}{4} \\ & + \; \rho g_z \frac{\pi D^2 L(t)}{4} + \langle \tau_{zz}\rangle\big|_{z=L(t)+\ell(t)} \frac{\pi D^2}{4} \\ & - \; \langle \tau_{zz}\rangle\big|_{z=\ell(t)} \frac{\pi D^2}{4} \; + \; \langle \tau_{rz}\rangle\big|_{r=D/2}\, \pi D L(t) \end{aligned} \tag{193}$$

Neglecting the viscous stresses at the entrance and exit of the control volume, along with the gravitational term, leads to

$$0 = -\left(\frac{\langle p\rangle\big|_{z=L(t)+\ell(t)} \; - \; \langle p\rangle\big|_{z=\ell(t)}}{L(t)} \right) + \frac{4\langle \tau_{rz}\rangle\big|_{r=D/2}}{D} \tag{194}$$

This result leads to the estimate given by

$$\nabla p = \mathbf{O}\left(\frac{4\langle \tau_{rz}\rangle\big|_{r=D/2}}{D} \right) \tag{195}$$

and when used in Eq. (191) we obtain

$$\text{Restriction:}\; (\omega_A - x_A)\frac{4\langle \tau_{rz}\rangle\big|_{r=D/2}}{pD} \ll \frac{x_A x_B \mathbf{v}_A}{\mathcal{D}_{AB}} \tag{196}$$

At this point we can extract an estimate of the wall shear stress given by Eq. (185) to obtain

$$(\omega_A - x_A)\frac{\rho_A C_A}{pD} \ll \frac{x_A(1-x_A)}{\mathcal{D}_{AB}} \tag{197}$$

and use of Eq. (158) to estimate the pressure leads to the constraint given by

$$\text{Constraint:}\qquad \frac{x_A(1-x_A)}{\omega_A(\omega_A - x_A)}\frac{CD}{\mathcal{D}_{AB}} \gg 1 \tag{198}$$

This constraint is similar to that given by Eq. (188); however, the left hand side does not tend to zero as x_A approaches one.

Local acceleration

We now direct our attention to the last of the four restrictions given by Eqs. (154), and we express the restriction associated with the local acceleration as

$$\text{Restriction:}\quad p^{-1}\rho_A\left(\frac{\partial \mathbf{u}_A}{\partial t}\right) \ll \frac{x_A x_B \mathbf{v}_A}{\mathcal{D}_{AB}} \tag{199}$$

An estimate of the local acceleration is given by

$$\frac{\partial \mathbf{u}_A}{\partial t} = \mathbf{O}\left(\frac{\mathbf{u}_A}{t^*}\right) \tag{200}$$

in which t^* is the characteristic time associated with the process illustrated in Fig. 8. for a binary system in which $\mathbf{v}_B = 0$ we can relate the species velocity to the diffusion velocity by

$$\mathbf{v}_A = \frac{\mathbf{u}_A}{1-\omega_A} \tag{201}$$

Use of Eq. (200) and Eq. (201) in the restriction given by Eq. (201) provides

$$1 \ll \frac{x_A(1-x_A)}{\rho_A \mathcal{D}_{AB}}\frac{pt^*}{1-\omega_A} \tag{202}$$

and when the pressure is estimated by Eq. (158) we obtain the following constraint:

$$\text{Constraint:}\qquad \frac{x_A(1-x_A)}{\omega_A(1-\omega_A)}\frac{C^2\, t^*}{\mathcal{D}_{AB}} \gg 1 \tag{203}$$

In general it is very, very difficult to violate this constraint.

Convective acceleration

The restriction associated with the convective acceleration term in Eq. (154d), subject to the condition of a binary mixture with $\mathbf{v}_B = 0$, provides the special case given by

$$\text{Restriction:}\; p^{-1}\rho_A\left(\mathbf{v}_A\cdot\nabla\mathbf{u}_A + \mathbf{u}_A\cdot\nabla\mathbf{v}\right) \ll \frac{x_A x_B \mathbf{v}_A}{\mathcal{D}_{AB}} \tag{204}$$

In this case the characteristic length associated with $\nabla\mathbf{u}_A$ and $\nabla\mathbf{v}$ is $L(t)$ illustrated in Fig. 8. One can express $\mathbf{v}_A$ and $\mathbf{u}_A$ in terms of the mass average velocity to obtain

$$\mathbf{v}_A = \frac{\mathbf{v}}{\omega_A}\,,\; \mathbf{u}_A = \frac{\mathbf{v}(1-\omega_A)}{\omega_A} \tag{205}$$

and this allows us to represent Eq. (204) in the form

$$p^{-1}\rho_A\left\{ \frac{\mathbf{v}}{\omega_A}\cdot\nabla\left[\frac{\mathbf{v}(1-\omega_A)}{\omega_A}\right] + \frac{\mathbf{v}(1-\omega_A)}{\omega_A}\cdot\nabla\mathbf{v} \right\} \ll \frac{x_A x_B \mathbf{v}}{\omega_A \mathcal{D}_{AB}} \tag{206}$$

Using $L(t)$ in the estimates of the gradients suggests the following form

$$\frac{\rho_A}{p}\frac{\mathbf{v}\mathbf{v}}{L(t)}\frac{(1-\omega_A)}{\omega_A^2}\left[1+\mathbf{O}(\omega_A)\right] \ll \frac{x_A x_B \mathbf{v}}{\omega_A \mathcal{D}_{AB}} \tag{207}$$

At this point we make use of Eq. (158) for the pressure in order to express this result in the form

$$\text{Constraint: } \frac{x_A(1-x_A)}{\left(1-\omega_A\right)}\frac{L(t)C}{M\,\mathscr{D}_{AB}} \gg \left[1+\mathbf{O}\left(\omega_A\right)\right] \tag{208}$$

in which M is the Mach number defined by

$$M = \frac{\mathrm{v}}{C} \tag{209}$$

Clearly this constraint will always be satisfied for the process illustrated in Fig. 8.

A special form of the Stefan-Maxwell equations

When the constraints indicated by Eqs. (168), (188), (198), (203) and (208) are satisfied, we expect that Eq. (164) will indeed be a valid approximation for the species A momentum equation that we repeat here as

$$0 = -\nabla x_A - \frac{x_A x_B \mathbf{v}_A}{\mathscr{D}_{AB}} \tag{210}$$

This can be used to express the molar flux of species A in the form

$$c_A \mathbf{v}_A = \mathbf{N}_A = -\frac{c\mathscr{D}_{AB}}{x_B}\nabla x_A \tag{211}$$

and for the one-dimensional process illustrated in Fig. 8 we have

$$N_{Az} = -\frac{c\,\mathscr{D}_{AB}}{x_B}\frac{d\,x_A}{dz} \tag{212}$$

Other special forms of the Stefan-Maxwell equations are given by Whitaker (2009).

2.8 Knudsen diffusion

One crucial constraint leading to the Stefan-Maxwell equations given by Eqs. (146) is the constraint on the mean free path indicated by Eq. (179). When that constraint is satisfied we are assured that molecule-molecule collisions are *much more numerous* than molecule-wall collisions. When the inverse of that constraint is valid, i.e., when

$$\ell_A \gg D \tag{213}$$

we have the situation illustrated in Fig. 10 where we have shown a single molecule-molecule collision and many molecule-wall collisions. As the mean free path becomes large relative to the tube diameter, D, the diffusive force becomes negligible, i.e., $\mathbf{P}_{AB} \to 0$ and the simplification leading from Eq. (131) to Eqs. (143) and (146) is no longer valid. This requires that we return to Eq. (131) in the form given by

$$\begin{gathered}\frac{\partial}{\partial t}\left(\rho_A \mathbf{v}_A\right)+\nabla\cdot\left(\rho_A\mathbf{v}_A\mathbf{v}_A\right)\\ = \rho_A\,\mathbf{g} - \nabla p_A + \nabla\cdot\boldsymbol{\tau}_A\,, A = 1,2...,N\end{gathered} \tag{214}$$

in which the term $r_A\mathbf{v}_A$ has been discarded with the idea that the influence of chemical reactions can be ignored. In addition, we have replaced $\mathbf{b}_A$ with $\mathbf{g}$ with the idea that gravity is the only body force. At this point we make use of the macroscopic momentum balance associated with Eq. (214) in order to obtain

$$\begin{aligned}\frac{d}{dt}\int_{\mathscr{V}}\rho_A\mathbf{v}_A\,dV + \int_{\mathscr{A}}\rho_A\mathbf{v}_A\mathbf{v}_A\cdot\mathbf{n}\,dA &= \int_{\mathscr{V}}\rho_A\,\mathbf{g}\,dV\\ &- \int_{\mathscr{A}}\mathbf{n}\,p_A\,dA + \int_{\mathscr{A}}\mathbf{n}\cdot\boldsymbol{\tau}_A\,dA\end{aligned} \tag{215}$$

Here $\mathscr{V}$ represents the control volume illustrated in Fig. 10 and $\mathscr{A}$ represents the surface of that control volume. The component of this equation in the z-direction is given by

$$\begin{aligned}&\frac{d}{dt}\int_{\mathscr{V}}\rho_A\mathbf{v}_A\cdot\mathbf{k}\,dV + \int_{\mathscr{A}}\rho_A\mathbf{k}\cdot\mathbf{v}_A\mathbf{v}_A\cdot\mathbf{n}\,dA\\ &= \int_{\mathscr{V}}\rho_A\,\mathbf{g}\cdot\mathbf{k}\,dV - \int_{\mathscr{A}}\mathbf{n}\cdot\mathbf{k}\,p_A\,dA + \int_{\mathscr{A}}\mathbf{n}\cdot\boldsymbol{\tau}_A\cdot\mathbf{k}\,dA\end{aligned} \tag{216}$$

and for a steady, uniform flow this simplifies to

$$0 = \int_{\mathscr{V}}\rho_A\,\mathbf{g}\cdot\mathbf{k}\,dV - \int_{\mathscr{A}}\mathbf{n}\cdot\mathbf{k}\,p_A\,dA + \int_{\mathscr{A}}\mathbf{n}\cdot\boldsymbol{\tau}_A\cdot\mathbf{k}\,dA \tag{217}$$

Evaluating the terms in this momentum balance leads to

$$\begin{aligned}0 &= \rho_A\,g_z\,\frac{\pi D^2 L}{4} - \left(\langle p_A\rangle\big|_{z=L} - \langle p_A\rangle\big|_{z=0}\right)\frac{\pi D^2}{4}\\ &+ \langle\tau_{Azz}\rangle\big|_{z=L}\frac{\pi D^2}{4} - \langle\tau_{Azz}\rangle\big|_{z=0}\frac{\pi D^2}{4}\\ &+ \langle\tau_{Arz}\rangle\big|_{r=D/2}\,\pi DL\end{aligned} \tag{218}$$

For a uniform flow we can impose the condition

$$\langle\tau_{Azz}\rangle\big|_{z=L} = \langle\tau_{Azz}\rangle\big|_{z=0} \tag{219}$$

so that Eq. (218) simplifies to

$$\begin{aligned}0 = \rho_A\,g_z\,\frac{\pi D^2 L}{4} &- \left(\langle p_A\rangle\big|_{z=L} - \langle p_A\rangle\big|_{z=0}\right)\frac{\pi D^2}{4}\\ &+ \langle\tau_{Arz}\rangle\big|_{r=D/2}\,\pi DL\end{aligned} \tag{220}$$

This momentum balance can be divided by $\pi D^2 L/4$ in order to obtain

$$0 = \rho_A\,g_z - \frac{\langle p_A\rangle\big|_{z=L} - \langle p_A\rangle\big|_{z=0}}{L} + \frac{4}{D}\langle\tau_{Arz}\rangle\big|_{r=D/2} \tag{221}$$

and we take the limit $L \to 0$ in order to express this result in the form

$$0 = \frac{\partial\langle p_A\rangle}{\partial z} + \rho_A\,g_z + \frac{4}{D}\langle\tau_{Arz}\rangle\big|_{r=D/2} \tag{222}$$

At this point we refer to Eqs. (180) through (182) to *estimate* the partial stress as

$$\langle\tau_{Arz}\rangle\big|_{r=D/2} = \frac{1}{4}\rho_A C_A\,\mathrm{v}_{Az}\big|_{r=D/2} \tag{223}$$

One must remember that Eq. (180) is based on the approximation given by Eq. (176) and that the latter is valid for an unbounded gas at equilibrium. For the process illustrated in Fig. 10, we can assume that both the velocity and the pressure will be uniform over any cross section of the tube, and this allows us to express Eq. (222) as

$$0 = \frac{\partial p_A}{\partial z} + \rho_A\,g_z + \frac{1}{D}\rho_A C_A\,\mathrm{v}_{Az} \tag{224}$$

In many cases, the following inequality is valid

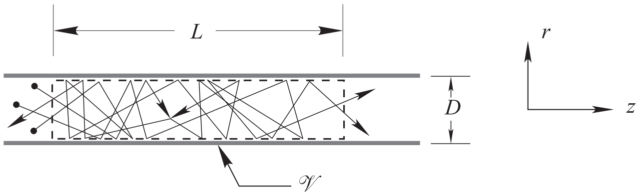


Fig. 10. Knudsen diffusion

$$g_z \ll \frac{1}{D} C_A \mathrm{v}_{Az} \tag{225}$$

and Eq. (224) simplifies to

$$0 = \frac{\partial p_A}{\partial z} + \frac{1}{D} \rho_A C_A \mathrm{v}_{Az} \tag{226}$$

The species mass density can be expressed in terms of the species molar concentration according to

$$\rho_A = c_A M_A \tag{227}$$

in which M_A is the molecular mass of species *A*. Use of this expression in Eq. (226) leads to

$$c_A \mathrm{v}_{Az} = -\frac{D}{M_A C_A} \frac{\partial p_A}{\partial z} \tag{228}$$

in which $c_A \mathrm{v}_{Az}$ is the molar flux often represented by N_{Az}. Expressing the partial pressure of species *A* in terms of the ideal gas law leads to

$$\frac{\partial p_A}{\partial z} = \frac{\partial (c_A RT)}{\partial z} = RT \frac{\partial c_A}{\partial z} \tag{229}$$

and use of this expression in Eq. (228) provides a result that can be expressed as

$$N_{Az} = -D_{A,K} \frac{\partial c_A}{\partial z}, \quad A = 1, 2, ..., N \tag{230}$$

The coefficient $D_{A,K}$ has units of m^2/s and it is known as the Knudsen diffusion coefficient for molecular species *A*. It is defined explicitly by

$$D_{A,K} = \frac{RT\,D}{M_A C_A}, \quad A = 1, 2, ..., N \tag{231}$$

Like the Stefan-Maxwell equations, this result has its origins in the species momentum equation, i.e., it is a *mechanical* result. Knudsen diffusion usually occurs in porous media where pores of small diameter are prevalent (Jackson, 1977, page 8).

2.9 Summary

In this section we have seen how the species momentum equations given by Eqs. (136) can be used to obtain the total momentum equation given by Eq. (143). In addition, we have shown how the species momentum equations can be used to produce the Stefan-Maxwell equations given by Eqs. (146). The restrictions that are required to produce the Stefan-Maxwell equations are given by Eqs. (154) and the constraints associated with those restrictions are developed for the Stefan diffusion tube illustrated in Fig. 8. The treatment of the species momentum equations is not a straightforward process. This is illustrated in the classic treatment of the Stefan diffusion tube, where one of the governing differential equations was discarded in favor of a plausible intuitive hypothesis. The Stefan-Maxwell equations describe mass transport when the diffusive force plays an important role in the species momentum equation. When the mean free path is large compared to the characteristic length associated with a system, the diffusive force becomes negligible and the species momentum equations become uncoupled. Under these circumstances the *N* species momentum equations lead to the Knudsen diffusion equation.

The manipulation of the species momentum equations is a crucial element of chemical engineering analysis since those equations are required to determine the species velocities, $\mathbf{v}_A$, $\mathbf{v}_B$, …, $\mathbf{v}_N$. In turn, knowledge of the species velocities is essential for the determination of adsorption and desorption rates, inter-phase transport rates, and heterogeneous reaction rates. These processes will be considered in the next section.

3. The interface between two phases

In Sec. 1 of this work, the interface between physics and chemical engineering was explored from the point of view of the laws of mechanics. Constructing a *connection* between the perspective of a physicist and the perspective of a chemical engineer is based on the work of Euler and Cauchy. Understanding Euler's laws, Cauchy's equations, and the Euler cut principle allows the chemical engineer to create a fundamental understanding of fluid mechanics. What is more important is that the work of Euler and Cauchy provides the framework for a study of multicomponent systems. In terms of mechanics, this leads to a method of determining the species velocities as outlined in the previous section.

3.1 Hierarchical systems

Most chemical engineering systems are hierarchical in nature, thus important processes take place at a variety of length scales. This perspective is shown in Fig. 11 where we have illustrated a large-scale chemical production system that may consist of several (in this case three) specialized chemical plants. Within one of these chemical plants we have illustrated a purification unit called a scrubber and we have further illustrated a bubble in the scrubber where mass transfer takes place. Finally, we have illustrated the gas-liquid interface in which the liquid

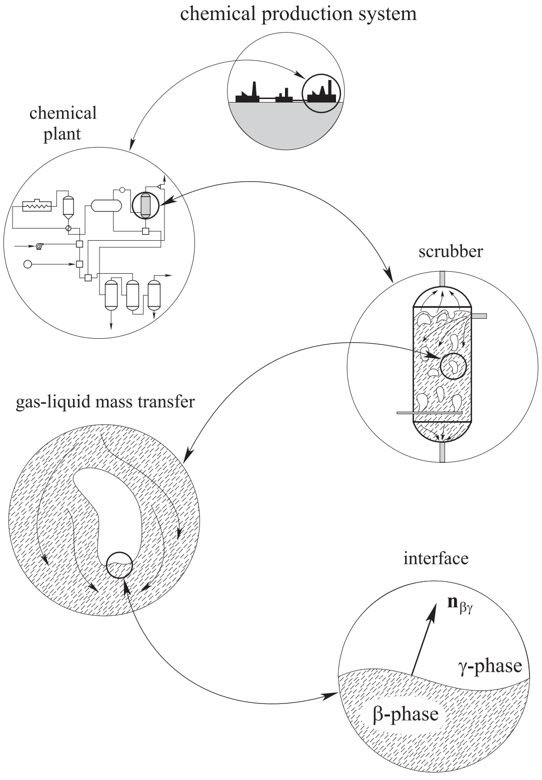


Fig. 11. Hierarchical systems

is identified as the β-phase and the gas is identified as the γ-phase. The orientation of the interface is identified by the unit normal vector, $\mathbf{n}_{\beta\gamma}$, that is directed from the β-phase toward the γ-phase. At every length scale illustrated in Fig. 11 there are challenging engineering problems associated with the purification of raw materials and the production of useful products. However, if *nothing happens* at the β–γ interface and the other interfaces within the entire system, *nothing happens* in the entire system! We explore this point of view in the following paragraphs.

3.2 Mass transport

The most dominant characteristic of a chemical species is its concentration, c_A with $A = 1, 2, \ldots, N$. If we could predict this concentration for all species of interest, many chemical engineering problems would be *solved problems*. Prediction of this concentration requires that we solve the species transport equation given earlier by Eq. (98) and repeated here as

$$\frac{\partial c_A}{\partial t} + \nabla \cdot \left(c_A \mathbf{v}_A \right) = R_A \ , A = 1, 2, .., N \tag{232}$$

Here $\mathbf{v}_A$ represents the species velocity for species A, and R_A represents the net molar rate of production (per unit volume) of species A owing to chemical reaction. In order to solve Eq. (232), in a general sense, we need to be able to determine the function

$$R_A = \mathscr{F}_A(c_A, c_B, ..., T) \tag{233}$$

along with the species velocity, $\mathbf{v}_A$, and an appropriate set of boundary conditions. The temperature will be determined by the *laws of thermodynamics* (Truesdell, 1969) while the species velocity will be determined by application of the *laws of mechanics* (Truesdell and Toupin, 1960). In order to focus attention of the net molar rate of production of species *A*, we ask the question: What would happen if all reaction rates were zero, i.e.,

$$R_A = R_B = R_C = R_D = \text{etc.} = 0 \tag{234}$$

Clearly the answer is that the earth would be a biologically inert sphere not at all like the planet with which we are familiar. Along the same lines, we can focus our attention of the species velocity and ask the question: What would happen if all species velocities were the same, i.e.,

$$\mathbf{v}_A = \mathbf{v}_B = \mathbf{v}_C = \mathbf{v}_D = \text{etc.} \tag{235}$$

If all molecular species had the same velocity, there would be *no mixing* and thus no chemical or biological reactions as indicated by Eq. (234). Clearly Eq. (232) is a *central issue* for chemical engineers and the determination of the species velocity and the net rate of production owing to chemical reactions is of the utmost importance.

The direct solution of Eq. (232) everywhere would lead to the prediction of concentration, c_A, the flux, $c_A\mathbf{v}_A$, and the rate of reaction, R_A. This, in turn, would provide the solution to many, many chemical engineering problems. However, the solution of Eq. (232) in the neighborhood of an interface is complicated by the fact that c_A, $\mathbf{v}_A$, and R_A change very rapidly in this region. For example, if there is significant adsorption at the interface between the β-phase and the γ-phase illustrated in Fig. 11, the concentration profile has the form illustrated in Fig. 12. The solution of Eq. (232) can be carried out in the interfacial region (Wood, *et al*., 2004) to predict c_A; however, the computation is quite complex and in general it is avoided by the construction of a jump condition for the β-γ interface. In this approach, the direct use of Eq. (232) is avoided and instead one makes use of governing equations for the β-phase and the γ-phase given by

$$\frac{\partial c_{A\beta}}{\partial t} + \nabla \cdot (c_{A\beta} \mathbf{v}_{A\beta}) = R_{A\beta} \ , \qquad A = 1, 2, 3, ..., N \ , \quad \text{in the } \beta\text{-phase} \tag{236}$$

$$\frac{\partial c_{A\gamma}}{\partial t} + \nabla \cdot (c_{A\gamma} \mathbf{v}_{A\gamma}) = R_{A\gamma} \ , \qquad A = 1, 2, 3, ..., N \ , \quad \text{in the } \gamma\text{-phase} \tag{237}$$

These equations are solved in both the homogeneous regions of the β and γ-phases and in the regions up to the dividing surface illustrated in Fig. 12. The boundary condition that joins these two transport equations is constructed in a manner that requires Eq. (232) to be satisfied *on the average* in the interfacial region. This leads to an interfacial flux boundary condition that can be derived using only undergradu-

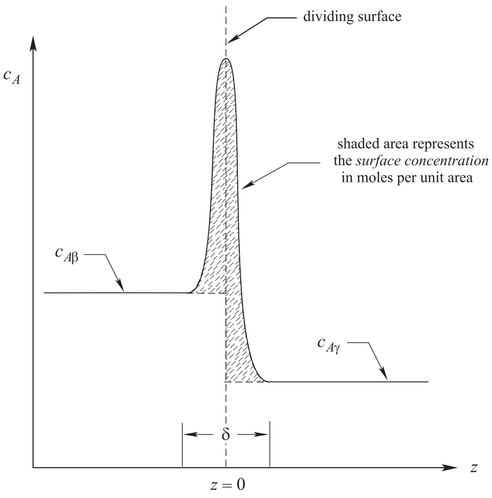


Fig. 12. Concentration distribution caused by adsorption at the β-γ interface.

ate *vector analysis* (Stein and Barcellos, 1992), and the result is given by (Whitaker, 1992).

$$\underbrace{\left.\frac{dc_{As}}{dt}\right|_{\mathbf{n}_{\beta\gamma}\cdot(\mathbf{w}\cdot\mathbf{n}_{\beta\gamma})}}_{\text{surface accumulation}} + \nabla_s\cdot\underbrace{(\mathbf{v}_{As}c_{As})}_{\text{surface transport}} + \underbrace{c_{As}(\nabla_s\cdot\mathbf{n}_{\beta\gamma})(\mathbf{w}\cdot\mathbf{n}_{\beta\gamma})}_{\text{effect of the changing surface area}}$$
$$= \underbrace{\left[c_{A\beta}(\mathbf{v}_{A\beta}-\mathbf{w}) - c_{A\gamma}(\mathbf{v}_{A\gamma}-\mathbf{w})\right]\cdot\mathbf{n}_{\beta\gamma}}_{\text{interfacial flus}} + \underbrace{R_{As}}_{\substack{\text{heterogeneous}\\ \text{reaction}}} ,$$
$$\text{at the } \beta\text{-}\gamma \text{ interface} \qquad (238)$$

When the interface can be treated as flat, the concentration profile illustrated in Fig. 12 leads to the surface concentration given by

$$c_{As} = \int\limits_{z=-\delta/2}^{z=0} \left(c_A - c_{A\beta}\right)dz + \int\limits_{z=0}^{z=\delta/2} \left(c_A - c_{A\gamma}\right)dz \qquad (239)$$

and the net rate of production owing to heterogeneous reaction, R_{As}, is defined in a similar manner. The boundary condition, or *jump condition* given by Eq. (238), provides a connection between the interfacial fluxes in the two phases, and to complete the formulation of this mass transfer process, we need a *connection* between the concentrations in the two phases. When the condition of *local thermodynamic equilibrium* is valid, the connection between the concentration in the two phases is given in terms of the equivalence of the chemical potentials, i.e.,

$$\mu_{A\beta} = \mu_{A\gamma} \; , A = 1,2,..,N \; , \text{at the } \beta\text{-}\gamma \text{ interface} \qquad (240)$$

The chemical potentials are functions of the state of the system, and Eq. (240) can be used to develop a relation between either the concentrations in the two phases or the mole fractions in the two phases. When the condition of local thermodynamic equilibrium is *not valid*, Eq. (238) can sometimes be replaced with an interfacial flux constitutive equation (Whitaker, 1999, Sec. 1.1.1; Wood, *et al*., 2004) that provides a connection between the concentrations.

In Eq. 238 we have used c_{As} to represent the *surface concentration* having units of moles *per unit area*. This concentration is sometimes referred to as the *excess surface concentration* and a graphical illustration of this concentration is illustrated in Fig. 12. The mean curvature of a surface is defined by

$$H = \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad (241)$$

where R_1 and R_2 are the principle radii of curvature. With the use of more advanced differential geometry (McConnell, 1957; Slattery, 1990) one can show that the surface gradient of the unit normal vector is equal to twice the mean curvature

$$\nabla_s \cdot \mathbf{n}_{\beta\gamma} = 2H \qquad (242)$$

in which H is given in terms of the principle radii of curvature by Eq. (241). Use of this result allows us to express the jump condition as

$$\underbrace{\left.\frac{dc_{As}}{dt}\right|_{\mathbf{n}_{\beta\gamma}\cdot(\mathbf{w}\cdot\mathbf{n}_{\beta\gamma})}}_{\text{surface accumulation}} + \underbrace{\nabla_s\cdot(\mathbf{v}_{As}c_{As})}_{\text{surface transport}} + \underbrace{c_{As}\,2H(\mathbf{w}\cdot\mathbf{n}_{\beta\gamma})}_{\text{effect of the changing surface area}}$$
$$= \underbrace{\left[c_{A\beta}(\mathbf{v}_{A\beta}-\mathbf{w}) - c_{A\gamma}(\mathbf{v}_{A\gamma}-\mathbf{w})\right]\cdot\mathbf{n}_{\beta\gamma}}_{\text{interfacial flus}} + \underbrace{R_{As}}_{\substack{\text{heterogeneous}\\ \text{reaction}}} ,$$
$$\text{at the } \gamma\text{-}\beta \text{ interface} \qquad (243)$$

in which we need to pay attention to the sign of the curvature, H. When $H = 0$ (flat surface) or when $\mathbf{w}\cdot\mathbf{n}_{\beta\gamma} = 0$ (zero speed of displacement), there is no changing surface area and $c_{As}\,2H(\mathbf{w}\cdot\mathbf{n}_{\beta\gamma})$ is equal to zero. For the case of expanding or contracting bubbles and drops, this term must be considered whenever the surface concentration, c_{As}, plays an important role in the jump condition. The first term on the right hand side of Eq. (243) represents the *interfacial transport* of species A from the β-phase to the γ-phase, while the second term represents the classic rate of *heterogeneous reaction*. Clearly the jump condition given by Eq. (243) is a *central issue* in the world of chemical engineering since it contains the phenomena of adsorption, surface transport, surface accumulation, interfacial mass transfer and heterogeneous reaction.

3.3 Adsorption/Desorption

If the β-phase is a *rigid solid phase* at which adsorption and/or desorption takes place, Eq. (243) for species A takes the special form given by (with $\mathbf{n}_{\beta\gamma} = -\mathbf{n}_{\gamma\beta}$)

$$\frac{\partial c_{As}}{\partial t} = c_{A\gamma}\mathbf{v}_{A\gamma}\cdot\mathbf{n}_{\gamma\beta} \; , \quad \text{at the } \gamma\text{-}\beta \text{ interface} \qquad (244)$$

This provides a boundary condition for Eq. (237) which we repeat here as

$$\frac{\partial c_{A\gamma}}{\partial t} + \nabla\cdot(c_{A\gamma}\mathbf{v}_{A\gamma}) = R_{A\gamma} \; , \text{ in the } \gamma\text{-phase} \qquad (245)$$

In order to connect the surface concentration, c_{As}, to the bulk concentration, $c_{A\gamma}$, we need to assume the condition of *local thermodynamic equilibrium* (see Eq. 240) or we need to develop an interfacial flux constitutive equation. If the condition of local thermodynamic equilibrium is valid and the adsorption isotherm is linear, the surface concentration is given by

Local equilibrium:

$$c_{As} = K_{eq} c_{A\gamma} \, , \text{ at the } \gamma\text{-}\beta \text{ interface} \tag{246}$$

Under these conditions the jump condition takes the form

$$K_{eq} \frac{\partial c_{A\gamma}}{\partial t} = c_{A\gamma} \mathbf{v}_{A\gamma} \cdot \mathbf{n}_{\gamma\beta} \, , \text{ at the } \gamma\text{-}\beta \text{ interface} \tag{247}$$

In this simple case of adsorption we see a connection between *mass transfer* (Eq. 245), *thermodynamics* (Eq. 246), *heat transfer* (K_{eq} is a function of temperature), and *mechanics* (Eqs. 143 and 146). If the condition of local thermodynamic equilibrium is not valid, one must develop an interfacial flux constitutive equation and the simplest case is the linear process described by

Non-equilibrium:

$$\frac{\partial c_{As}}{\partial t} = k_1 \, c_{A\gamma} - \, k_{-1} \, c_{As} \, , \text{at the } \gamma\text{-}\beta \text{ interface} \tag{248}$$

Use of this type of constitutive equation has been examined by Wood *et al*. (2004) in some detail.

3.4 Heterogeneous reaction

Here we again assume that the β-phase is rigid and we assume that the γ–β interface is a catalytic surface. We neglect surface transport and assume that the process is either *steady* or *quasi-steady* so that Eq. (243) simplifies to

$$0 = c_{A\gamma} \mathbf{v}_{A\gamma} \cdot \mathbf{n}_{\gamma\beta} + R_{As} \, , \quad \text{at the } \gamma\text{-}\beta \text{ interface}, A = 1, 2, ..., N \tag{249}$$

The heterogeneous rate of reaction, R_{As}, should depend on the *surface concentrations* (Bird *et al*., 2002, page 544) of the participating species, i.e., c_{As}, c_{Bs}, etc., and we express this idea as

$$R_{As} = R_{As}(c_{As}, c_{Bs}, ..., T) \, , A = 1, 2, ..., N \tag{250}$$

Here we see the need for a *connection* between the surface concentrations and the bulk concentrations at the γ–β interface. If the condition of *local thermodynamic equilibrium* is valid, Eq. (250) can be expressed as

$$R_{As} = R_{As}(c_{A\gamma}, c_{B\gamma}, ..., T) \, , A = 1, 2, ..., N \tag{251}$$

and the jump condition for heterogeneous reaction takes the form

$$c_{A\gamma} \mathbf{v}_{A\gamma} \cdot \mathbf{n}_{\gamma\beta} = - R_{As}(c_{A\gamma}, c_{B\gamma}, ..., T) \, , \quad \text{at the } \gamma\text{-}\beta \text{ interface} \, , A = 1, 2, ..., N \tag{252}$$

Here we should note that R_{As} represents the net rate of production of species A, thus the flux of species A from the γ-phase *toward* the β-phase is *positive* when R_{As} is *negative*. In this simple application of Eq. (243) to the case of heterogeneous reaction we see a connection between *mass transfer* (Eq. 245), *thermodynamics* (Eq. 251), *heat transfer* (R_{As} is a function of temperature), and *mechanics* (Eqs. 143 and 146). If local thermodynamic equilibrium is not valid, one may be confronted with a three-step process involving (1) a rate of adsorption, (2) a rate of reaction, and (3) a rate of desorption. In that case, concepts from Sec. 3.3 need to be incorporated into the analysis.

3.5 Interfacial mass transfer

When adsorption and heterogeneous reaction are negligible at a fluid-fluid interface, we have the apparently simple case of interfacial mass transfer and Eq. (243) simplifies to

$$c_{A\beta}(\mathbf{v}_{A\beta} - \mathbf{w}) \cdot \mathbf{n}_{\beta\gamma} = c_{A\gamma}(\mathbf{v}_{A\gamma} - \mathbf{w}) \cdot \mathbf{n}_{\beta\gamma} \, , \quad \text{at the } \beta - \gamma \text{ interface} \tag{253}$$

Here it is important to recognize that the speed of displacement of the β–γ interface, denoted by $\mathbf{w} \cdot \mathbf{n}_{\beta\gamma}$ can only be determined, in a general sense, by solving the equations of motion. This means that the speed of displacement of the interface illustrated in Fig. 12 is *part of the solution* of the fluid mechanical problem and not part of the problem statement. The hierarchical system illustrated in Fig. 11 is likely to contain many, many moving interfaces at which mass transfer takes place, and dealing with these moving interfaces represents a challenge that is generally ignored in texts on mass transfer. The moving boundary illustrated in Fig. 8 can be treated in a relatively simple manner (Bird *et al*., 2002, page 549) because the mass transfer process is quasi-steady. The process of diffusion with a moving boundary is discussed by Crank (1956, page 99) who has also provided a survey of methods for treating moving boundary problems (Crank, 1984).

As in the case of adsorption and the case of heterogeneous reaction, we need to impose either the condition of local thermodynamic equilibrium or we need to develop a model for the interfacial flux in order to connect $x_{A\beta}$ with $x_{A\gamma}$. If Eq. (240) is applicable, and the system is *linear*, we can use an equilibrium relation of the form

$$x_{A\beta} = K_A \, x_{A\gamma} \, , \text{equilibrium at the } \beta - \gamma \text{ interface} \tag{254}$$

in which K_A is the equilibrium coefficient. For *non-linear* systems, one must work with a general relation that can be expressed as

$$x_{A\beta} = \mathscr{F}(x_{A\gamma}) \, , \text{equilibrium at the } \beta - \gamma \text{ interface} \tag{255}$$

While interfacial flux constitutive equations, such as Eq. (248), are common in the treatment of adsorption/desorption phenomena and in the treatment of heterogeneous reactions, they are not for mass transfer process that can be described by Eq. (253). In this simple application of Eq. (243) to the case of interfacial mass transfer we again see a connection between *mass transfer* (Eq. 245), *thermodynamics* (Eq. 254), *heat transfer* (K_A is a function of temperature), and *mechanics* (Eqs. 143 and 146).

3.6 Summary

In this section we have examined three mass transfer processes that occur at phase interfaces, and all three of these processes are related by the species mass jump condition. We have seen how the species mass jump condition serves as a focal point for the connection of mass transfer, heat transfer, thermodynamics, and mechanics. As a focal point, the jump condition serves to *connect* various areas of chemical engineering that are often taught as separate and isolated subjects. This isolation appears in various forms and perhaps the most obvious form is visible in terms of the so-called special discipline of *chemical reaction engineering*. Other special disciplines are in the making; however, the physical processes in the world around us care little for special disciplines. Instead they are bound only by the laws of physics.

Conclusions

In this study we have examined the interface between physics and chemical engineering in terms of the subject of mechanics. *Connecting* the two different perspectives required a study of the work of Euler and Cauchy which, in turn, provided the basis for a study of the mechanics of multicomponent systems. Finally we examined a single equation, the *species mass jump condition*, that served to illustrate the *connections* between mass transfer, heat transfer, thermodynamics, and chemical reaction.

Nomenclature

$\mathscr{A}$	surface area of a fixed control volume, m^2
$\mathscr{A}_m(t)$	surface area of a material volume, m^2
$\mathscr{A}_a(t)$	surface area of an arbitrary moving control volume, m^2
$\mathscr{A}_A(t)$	surface area of a species A material volume, m^2
A	area, m^2
$\mathbf{b}$	total body force per unit mass, N/kg
$\mathbf{b}_i$	$i = 1, 2, \ldots, N$, body force exerted by a large, external body on the i^{th} mass point, N
$\mathbf{b}_{12}$	body force per unit mass exerted by body #2 on body #1, N/kg
$\mathbf{b}_{21}$	body force per unit mass exerted by body #1 on body #2, N/kg
c_A	molar concentration of species A, mole/m^3
$c_{A\beta}$	molar concentration of species A in the β-phase, mole/m^3
$c_{A\gamma}$	molar concentration of species A in the γ-phase, mole/m^3
c_{As}	surface concentration of species A associated with the β–γ interface, mole/m^2
C	speed of sound, m/s
C_A	speed of sound for species A, m/s
D	diameter, m
$\mathscr{D}_{AB}$	$\mathscr{D}_{BA}$, binary diffusion coefficient for species A and B, m^2/s
$D_{A,K}$	Knudsen diffusion coefficient for species A, m^2/s
$\mathbf{f}$	force, N
$\mathbf{f}_{12}$	force exerted by body #2 on body #1, N
$\mathbf{f}_{21}$	force exerted by body #1 on body #2, N
$\mathbf{f}_{ij}$	force exerted by the j^{th} mass point on the i^{th} mass point in a cloud of mass points, N
$\mathbf{g}$	gravitational body force per unit mass, N/kg
H	curvature, m^{-1}
$\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$	unit vectors
$\mathbf{I}$	unit tensor
K_{eq}	adsorption equilibrium coefficient, m
K_A	interphase equilibrium coefficient for species A
k_1	adsorption rate coefficient, m/s
k_{-1}	desorption rate coefficient, s^{-1}
ℓ_A	mean free path of species A, m
$L(t)$	diffusion path for the Stefan diffusion tube, m
M_A	molecular mass of species A, g/mole
m	mass, kg
m_A	mass per molecule of species A, kg/number
N_{JA}	chemical composition indicator
$\mathbf{N}_A$	$c_A\mathbf{v}_A$, molar flux of species A, mole/m^{2}s
$\mathbf{n}$	unit normal vector
n_A	number density of species A molecules
$\mathbf{n}_{\beta\gamma}$	$-\,\mathbf{n}_{\beta\gamma}$, unit normal vector directed from the β-phase to the γ-phase
$\mathbf{P}$	$\mathbf{I} - \mathbf{n}_{\beta\gamma}\,\mathbf{n}_{\beta\gamma}$, projection tensor
$\mathbf{P}_{AB}$	diffusive force per unit volume exerted by species B on species A, N/m^3
p	pressure, N/m^2
p_A	partial pressure of species A, N/m^2
$\mathbf{r}$	position vector, m
$\mathbf{r}_{\text{CM}}$	position vector locating the center of mass, m
r_A	net mass rate of production of species A owing to homogeneous reactions, kg/m^{3}s
R	gas constant, J/mole K
R_A	net molar rate of production of species A owing to homogeneous reactions, mole/m^{3}s
R_{As}	net rate of production of species A owing to heterogeneous reactions, mole/m^{2}s
t	time, s
t^*	characteristic time, s
$\mathbf{t}_{(\mathbf{n})}$	stress vector, N/m^2
$\mathbf{t}_{A(\mathbf{n})}$	stress vector for species A, N/m^2
$\mathbf{T}$	stress tensor, N/m^2
$\mathbf{T}_A$	stress tensor for species A, N/m^2
T_{ij}	(i, j = 1,2,3) components of the stress tensor, N/m^2
T	absolute temperature, K
$\mathbf{u}_A$	$\mathbf{v}_A - \mathbf{v}$, mass diffusion velocity, m/s
$\mathbf{v}_A$	velocity of species A, m/s

$\mathbf{v}$	$\sum_{A=1}^{A=N}\omega_A\mathbf{v}_A$, mass average velocity, m/s
$\mathbf{v}_{CM}$	velocity of the center of mass, m/s
$\mathbf{w}\cdot\mathbf{n}_{\beta\gamma}$	speed of displacement of the β–γ interface, m/s
$\mathcal{V}$	volume, m^3
$\mathcal{V}_m(t)$	volume of a body, m^3
$\mathcal{V}_a(t)$	volume of an arbitrary, moving control volume, m^3
$\mathcal{V}_A(t)$	volume of a species *A* body, m^3
V	volume, m^3
x_A	c_A / c, mole fraction of species *A*
$x_{A\beta}$	$c_{A\beta} / c_\beta$, mole fraction of species *A* in the β-phase
$x_{A\gamma}$	$c_{A\gamma} / c_\gamma$, mole fraction of species *A* in the γ-phase

Greek letters

∇	$\mathbf{i}\frac{\partial}{\partial x}+\mathbf{j}\frac{\partial}{\partial y}+\mathbf{k}\frac{\partial}{\partial z}$, gradient operator, m^{-1}
∇_s	$\mathbf{P}\cdot\nabla$, surface gradient operator, m^{-1}
γ_A	activity coefficient ($\gamma_A \to 1$ as $x_A \to 1$)
ρ_A	mass density of species *A*, kg/m^3
ρ	total mass density, kg/m^3
τ	viscous stress tensor, N/m^2
τ_A	viscous stress tensor for species *A*, N/m^2
μ	viscosity, N/m^2s
μ_A	chemical potential for species *A*, J/mol
ω_A	ρ_A / ρ, mass fraction of species *A*

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Appendix A. Influence of Surface Forces

In our analysis of body forces and central forces in Sec. 1.3, we neglected the influence of surface forces in order to keep the analysis as simple as possible. In this appendix we include the effect of surface forces in order to demonstrate that they have no influence on our conclusions concerning central forces. We begin the analysis with Cuts I and II shown in Fig. 4 and apply Euler's first law to obtain

$$\text{Cut I}: \frac{d}{dt}\int_{\mathscr{V}_{\text{I}}(t)} \rho_1\,\mathbf{v}_1\,dV = \int_{\mathscr{V}_{\text{I}}(t)} \rho_1\,\mathbf{b}_{12}\,dV + \int_{\mathscr{V}_{\text{I}}(t)} \rho_1\,\mathbf{b}_{13}\,dV + \int_{\mathscr{A}_{\text{I}}(t)} \mathbf{t}_{(\mathbf{n})1}\,dA \tag{A1}$$

$$\text{Cut II}: \frac{d}{dt}\int_{\mathscr{V}_{\text{II}}(t)} \rho_2\,\mathbf{v}_2\,dV = \int_{\mathscr{V}_{\text{II}}(t)} \rho_2\,\mathbf{b}_{21}\,dV + \int_{\mathscr{V}_{\text{II}}(t)} \rho_2\,\mathbf{b}_{23}\,dV + \int_{\mathscr{A}_{\text{II}}(t)} \mathbf{t}_{(\mathbf{n})2}\,dA \tag{A2}$$

At this point we introduce the new form of Cut III illustrated in Fig. 1A. In this case the cylinder joining the two spherical portions of the cut is arbitrarily small and makes no contribution to either the volume or area integrals. Under these circumstances the application of Euler's first law to Cut III leads to

$$\frac{d}{dt}\left[\int_{\mathscr{V}_{\text{I}}(t)} \rho_1\,\mathbf{v}_1\,dV + \int_{\mathscr{V}_{\text{II}}(t)} \rho_2\,\mathbf{v}_2\,dV\right] = \int_{\mathscr{V}_{\text{I}}(t)} \rho_1\,\mathbf{b}_{13}\,dV + \int_{\mathscr{V}_{\text{II}}(t)} \rho_2\,\mathbf{b}_{23}\,dV + \int_{\mathscr{A}_{\text{I}}(t)} \mathbf{t}_{(\mathbf{n})1}\,dA + \int_{\mathscr{A}_{\text{II}}(t)} \mathbf{t}_{(\mathbf{n})2}\,dA \tag{A3}$$

Use of Eqs. (A1) and (A2) in this result immediately leads to

$$\int_{\mathscr{V}_{\text{I}}(t)} \rho_1\,\mathbf{b}_{12}\,dV + \int_{\mathscr{V}_{\text{II}}(t)} \rho_2\,\mathbf{b}_{21}\,dV = 0 \tag{A4}$$

This is Eq. (39) which provides Newton's third law given earlier by Eq. (42). Here we see that the inclusion of surface forces does not alter our conclusion about the "equal and opposite" nature of the body forces associated with the system shown in Fig. 1A.

Application of Euler's second law, including surface forces, to Cuts I and II shown in Fig. 4 leads to

$$\text{Cut I}: \frac{d}{dt}\int_{\mathscr{V}_{\text{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{v}_1\,dV = \int_{\mathscr{V}_{\text{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{b}_{12}\,dV + \int_{\mathscr{V}_{\text{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{b}_{13}\,dV + \int_{\mathscr{A}_{\text{I}}(t)} \mathbf{r}_1\times\mathbf{t}_{(\mathbf{n})1}\,dA \tag{A5}$$

$$\text{Cut II}: \frac{d}{dt}\int_{\mathscr{V}_{\text{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{v}_2\,dV = \int_{\mathscr{V}_{\text{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{b}_{21}\,dV + \int_{\mathscr{V}_{\text{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{b}_{23}\,dV + \int_{\mathscr{A}_{\text{I}}(t)} \mathbf{r}_2\times\mathbf{t}_{(\mathbf{n})2}\,dA \tag{A6}$$

We can now apply Euler's second law to Cut III shown in Fig. 1A to obtain

$$\text{Cut III}: \frac{d}{dt}\left[\int_{\mathscr{V}_{\text{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{v}_1\,dV + \int_{\mathscr{V}_{\text{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{v}_2\,dV\right] = \int_{\mathscr{V}_{\text{I}}(t)} \mathbf{r}_1\times\rho_1\,\mathbf{b}_{13}\,dV + \int_{\mathscr{V}_{\text{II}}(t)} \mathbf{r}_2\times\rho_2\,\mathbf{b}_{23}\,dV + \int_{\mathscr{A}_{\text{I}}(t)} \mathbf{r}_1\times\mathbf{t}_{(\mathbf{n})1}\,dA + \int_{\mathscr{A}_{\text{I}}(t)} \mathbf{r}_2\times\mathbf{t}_{(\mathbf{n})2}\,dA \tag{A7}$$

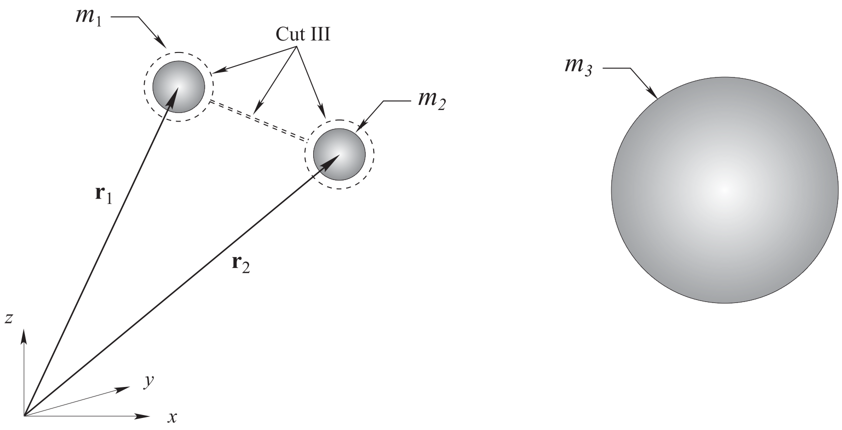

Fig. 1A. Three body process

Here we have again made use of the fact that the portion of the control volume connecting the two spheres makes a negligible contribution to either the area integrals or the volume integrals in Euler's second law. Use of Eqs. (A5) and (A6) in Eq. (A7) leads to the result given earlier by Eq. (47) that we repeat here as

$$\int_{\mathscr{V}_I(t)} \mathbf{r}_1 \times \rho_1 \mathbf{b}_{12}\, dV + \int_{\mathscr{V}_{II}(t)} \mathbf{r}_2 \times \rho_2 \mathbf{b}_{21}\, dV = 0 \tag{A8}$$

At this point we can follow the original analysis to obtain Eq. (50) and apply the development in Appendix B to obtain the restriction given by Eq. (51). Application of this restriction yields Eq. (52) which in turn provides the central force law given by Eq. (56).

Appendix B. Central Force Law

Deciding when some quantity is "small enough" so that it can be discarded is not an easy task. In this appendix we consider the analysis that led from Eq. (50) to Eq. (51) and then to the central force law represented by Eq. (56). We begin with Eq. (50)

$$\left[(\mathbf{r}_{\mathrm{CM}})_1 - (\mathbf{r}_{\mathrm{CM}})_2\right]\times \mathbf{f}_{12} + \left[\int_{\mathscr{V}_I(t)} \tilde{\mathbf{r}}_1 \times \rho_1 \mathbf{b}_{12}\, dV + \int_{\mathscr{V}_{II}(t)} \tilde{\mathbf{r}}_2 \times \rho_2 \mathbf{b}_{21}\, dV\right] = 0 \tag{B1}$$

and make use of the following nomenclature

$$\left[(\mathbf{r}_{\mathrm{CM}})_1 - (\mathbf{r}_{\mathrm{CM}})_2\right] = \mathbf{R} \tag{B2a}$$

$$\mathbf{f}_{12} = \mathbf{F} \tag{B2b}$$

$$\int_{\mathscr{V}_I(t)} \tilde{\mathbf{r}}_1 \times \rho_1 \mathbf{b}_{12}\, dV + \int_{\mathscr{V}_{II}(t)} \tilde{\mathbf{r}}_2 \times \rho_2 \mathbf{b}_{21}\, dV = \mathbf{D} \tag{B2c}$$

to express Eq. (B1) as

$$\mathbf{R}\times\mathbf{F} + \mathbf{D} = 0 \tag{B3}$$

Here we would like to know when the vector **D** can be discarded in order to simplify this result. A plausible intuitive hypothesis (Birkhoff, 1960) associated with this simplification is given by

Assumption: $\mathbf{R}\times\mathbf{F} = 0$ (B4)

however, we cannot discard **D** as being small compared to **R** x **F** since Eq. (B3) requires that **D** and **R** x **F** are the *same order of magnitude*. This type of problem has been considered before (Whitaker, 1988), and we will follow the procedure suggested in that earlier work. This requires that we *decompose* **F** into a part that is parallel to **R** and a part that is perpendicular to **R**

$$\mathbf{F} = \underbrace{\mathbf{F}_{=}}_{\text{parallel part}} + \underbrace{\mathbf{F}_{\perp}}_{\text{perpendicular part}} \tag{B5}$$

On the basis of this decomposition, we see that Eq. (B3) provides the two results given by

$$\mathbf{R}\times\mathbf{F}_{=} = 0 \tag{B6a}$$

$$\mathbf{R}\times\mathbf{F}_{\perp} + \mathbf{D} = 0 \tag{B6b}$$

This allows us to *estimate* $\mathbf{F}_{\perp}$ as

$$\mathbf{F}_{\perp} = \frac{\mathbf{O}(\mathbf{D})}{\mathbf{O}(\mathbf{R})} \tag{B7}$$

in which **O** indicates an order of magnitude estimate. If $\mathbf{F}_{\perp}$ is small relative to $\mathbf{F}_{=}$, and if small causes give rise to small effects, we can replace $\mathbf{F}_{=}$ with **F** and Eq. (B6a) leads to the central force law given as Eq. (56). In order to develop the conditions that must be satisfied in order that $\mathbf{F}_{\perp}$ be negligible compared to $\mathbf{F}_{=}$, we impose the inequality given by

Restriction: $\mathbf{F}_{=} \gg \mathbf{F}_{\perp}$ (B8)

In terms of the estimate given by Eq. B7 this leads to

$$\mathbf{F}_{=} \gg \frac{\mathbf{O}(\mathbf{D})}{\mathbf{O}(\mathbf{R})} \tag{B9}$$

and because of the constraint given by Eq. B8 we can express this result as

$$\mathbf{F} \gg \frac{\mathbf{O}(\mathbf{D})}{\mathbf{O}(\mathbf{R})} \tag{B10}$$

Making use of the definitions given by Eqs. (B2) we have

$$\mathbf{O}(\mathbf{f}_{12}) \gg \frac{\mathbf{O}\left[\int_{\mathscr{V}_I(t)} \tilde{\mathbf{r}}_1 \times \rho_1 \mathbf{b}_{12}\, dV + \int_{\mathscr{V}_{II}(t)} \tilde{\mathbf{r}}_2 \times \rho_2 \mathbf{b}_{21}\, dV\right]}{\mathbf{O}\left(\left[(\mathbf{r}_{\mathrm{CM}})_1 - (\mathbf{r}_{\mathrm{CM}})_2\right]\right)} \tag{B11}$$

On the basis of Eqs. (40) we obtain the estimates

$$\int_{\mathscr{V}_I(t)} \tilde{\mathbf{r}}_1 \times \rho_1 \mathbf{b}_{12}\, dV = \mathbf{O}(\tilde{\mathbf{r}}_1)\mathbf{f}_{12} \,,$$

$$\int_{\mathscr{V}_{\mathrm{II}}(t)} \tilde{\mathbf{r}}_2 \times \rho_2\, \mathbf{b}_{21}\, dV \;=\; \mathbf{O}\big(\tilde{\mathbf{r}}_2\big)\mathbf{f}_{21} \qquad \text{(B12)}$$

in which $\mathbf{f}_{12} = \mathbf{f}_{21}$. Use of these two estimates, along with Eq. (42), in Eq. (B11) leads to the constraint given by

$$\text{Constraint:} \quad \frac{\mathbf{O}(\tilde{\mathbf{r}}_1) \;+\; \mathbf{O}(\tilde{\mathbf{r}}_2)}{\mathbf{O}\big[(\mathbf{r}_{\mathrm{CM}})_1 \;-\; (\mathbf{r}_{\mathrm{CM}})_2\big]} \ll 1 \qquad \text{(B13)}$$

This would appear to be a general constraint associated with "mass point mechanics".

Appendix C. Cauchy's Lemma

In this development, we begin with Eq. (27) and apply it to the *body* illustrated in Fig. 1C. This leads to

$$\begin{aligned} \frac{d}{dt}\int_{\mathscr{V}_m(t)} \rho\,\mathbf{v}\, dV &= \int_{\mathscr{V}_m(t)} \rho\,\mathbf{b}\, dV \\ &+ \int_{A_n(t)} \mathbf{t}_{(\mathbf{n}_1)}\, dA + \int_{A_n(t)} \mathbf{t}_{(\mathbf{n}_2)}\, dA + \int_{A_{strip}(t)} \mathbf{t}_{(\boldsymbol{\mu})}\, dA \end{aligned} \qquad \text{(C1)}$$

in which $A_n(t)$ represents the area of the two parallel surfaces and $A_{strip}(t)$ represents the area of the connecting strip having a unit normal $\boldsymbol{\mu}$. In terms of average quantities, this form of Euler's first law reduces to

$$\begin{aligned} \frac{d}{dt}\big[\langle \rho\,\mathbf{v}\rangle\, \Delta L\, A_n(t)\big] &= \big[\langle \rho\,\mathbf{b}\rangle\, \Delta L\, A_n(t)\big] + \int_{A_n(t)} \mathbf{t}_{(\mathbf{n}_1)}\, dA \\ &+ \int_{A_n(t)} \mathbf{t}_{(\mathbf{n}_2)}\, dA \;+\; \langle \mathbf{t}_{(\boldsymbol{\mu})}\rangle\, A_{strip}(t) \end{aligned} \qquad \text{(C2)}$$

Here the volume averages are represented explicitly by

$$\begin{aligned} \int_{\mathscr{V}_m(t)} \rho\,\mathbf{v}\, dV &= \langle \rho\,\mathbf{v}\rangle \Delta L\, A_n(t)\,, \\ \int_{\mathscr{V}_m(t)} \rho\,\mathbf{b}\, dV &= \langle \rho\,\mathbf{b}\rangle \Delta L\, A_n(t) \end{aligned} \qquad \text{(C3)}$$

while the area average of the connecting strip has been expressed as

$$\int_{A_{strip}(t)} \mathbf{t}_{(\boldsymbol{\mu})}\, dA = \langle \mathbf{t}_{(\boldsymbol{\mu})}\rangle A_{strip}(t) \qquad \text{(C4)}$$

For the limiting case in which the thickness of the slab tends to zero, we have

$$\Delta L\, A_n(t) \to 0,\; A_{strip}(t) \to 0,\; as\;\; \Delta L \to 0 \qquad \text{(C5)}$$

and Eq. (C2) reduces to

$$0 = \int_{A_n(t)} \Big[\mathbf{t}_{(\mathbf{n}_1)} \;+\; \mathbf{t}_{(\mathbf{n}_2)}\Big] dA\,,\; \Delta L \to 0 \qquad \text{(C6)}$$

Since the limits of integration are arbitrary, the only non-trivial solution to this result is given by

$$\mathbf{t}_{(\mathbf{n}_1)} = -\,\mathbf{t}_{(\mathbf{n}_2)} \qquad \text{(C7)}$$

Traditionally, one uses $\mathbf{n}_1 = \mathbf{n}$ and $\mathbf{n}_1 = -\,\mathbf{n}$ so that this result takes the form given by

$$\text{Cauchy's lemma}^4 \quad \mathbf{t}_{(\mathbf{n})} = -\,\mathbf{t}_{(-\mathbf{n})} \qquad \text{(C8)}$$

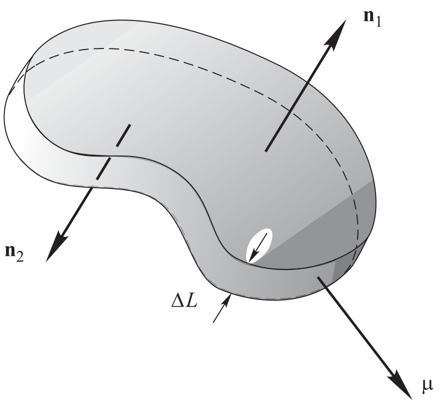

Fig. 1C. Body having the form of a slab

One can easily become confused when discussing the sign of a particular component of the stress vector acting on a particular surface, and the careful use of Eq. (C8) will help to avoid this confusion.

Appendix D. Cauchy's Fundamental Theorem

In Appendix C we learned something very important about the stress vector by applying Euler's first law to the slab illustrated in Fig. 1C, and we can learn more with an application to the tetrahedron shown in Fig. 1D. One should think of the tetrahedron as a *body* cut out of a distinct body according to the Euler cut principle.

The stresses shown in Fig. 1D are identified in a consistent manner, i.e., $\mathbf{t}_{(\mathbf{n})}$ represents the vector force per unit area acting on a surface having an unit normal $\mathbf{n}$. The unit normal vectors for the three coordinate surfaces shown in Fig. 1D are $-\mathbf{i}$, $-\mathbf{j}$, and $-\mathbf{k}$ respectively, thus the stress vectors acting on the coordinate surfaces are identified as $\mathbf{t}_{(-\mathbf{i})}$, $\mathbf{t}_{(-\mathbf{j})}$, and $\mathbf{t}_{(-\mathbf{k})}$ while the stress vector acting on the oblique surface is identified as $\mathbf{t}_{(\mathbf{n})}$. The areas, normal vectors, and stress vectors associated with the tetrahedron shown in Fig. 1D are listed in Table D-1. The oblique area is designated by ΔA, and the areas of the coordinate surfaces are identified in terms of the coordinate that is constant over the surface. Thus the coordinate surface coincident with the *y*-*z* plane is identified as ΔA_x and we will refer to this surface as the *x*-surface. While this nomenclature is convenient for the identification of the coordinate surfaces of the tetrahedron shown in Fig. 1D, one must be careful to remember that ΔA_x *does not represent the component of a vector*.

We can apply Eq. (27) to the tetrahedron and express the result as

$$\begin{aligned} \frac{d}{dt}\int_{\Delta V} \rho\,\mathbf{v}\, dV &= \int_{\Delta V} \rho\,\mathbf{b}\, dV + \int_{\Delta A} \mathbf{t}_{(\mathbf{n})}\, dA \\ &+ \int_{\Delta A_x} \mathbf{t}_{(-\mathbf{i})}\, dA + \int_{\Delta A_y} \mathbf{t}_{(-\mathbf{j})}\, dA + \int_{\Delta A_z} \mathbf{t}_{(-\mathbf{k})}\, dA \end{aligned} \qquad \text{(D1)}$$

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[4] James, G. and James, R.C. 1959, *Mathematics Dictionary* (multilingual edition), "lemma, a theorem proved for the use in the proof of another theorem", D. van Nostrand Co., Inc., New York.

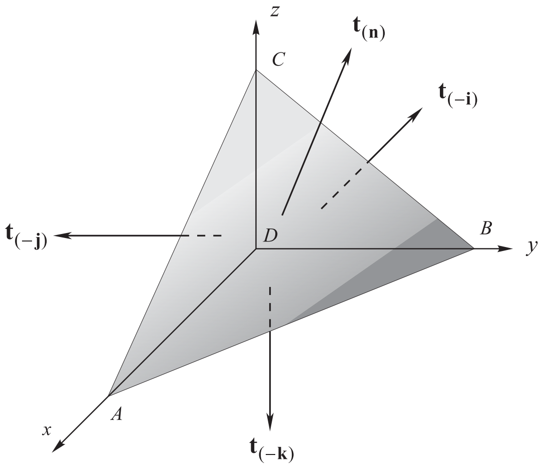

Fig.1D. Stresses acting on a tetrahedron.

Table D-1. Stresses acting on a tetrahedron

Plane	Area	Normal	Stress vector
ABC	ΔA	$\mathbf{n}$	$\mathbf{t}_{(\mathbf{n})}$
BCD	ΔA_x	$-\,\mathbf{i}$	$\mathbf{t}_{(-\mathbf{i})}$
ADC	ΔA_y	$-\,\mathbf{j}$	$\mathbf{t}_{(-\mathbf{i})}$
ABD	ΔA_z	$-\,\mathbf{k}$	$\mathbf{t}_{(-\mathbf{k})}$

Here we have used ΔV to represent the volume of the tetrahedron while the four areas are represented by ΔA, ΔA_x, ΔA_y and ΔA_z. In terms of average quantities, Euler's first law takes the form

$$\frac{d}{dt}\big[\langle\rho\,\mathbf{v}\rangle\,\Delta V\big] = \big[\langle\rho\,\mathbf{b}\rangle\,\Delta V\big] + \langle\mathbf{t}_{(\mathbf{n})}\rangle\Delta A + \langle\mathbf{t}_{(-\mathbf{i})}\rangle\Delta A_x + \langle\mathbf{t}_{(-\mathbf{j})}\rangle\Delta A_y + \langle\mathbf{t}_{(-\mathbf{k})}\rangle\Delta A_z \tag{D2}$$

in which volume averages are expressed as

$$\frac{d}{dt}\int_{\Delta V}\rho\,\mathbf{v}\,dV = \frac{d}{dt}\big[\langle\rho\,\mathbf{v}\rangle\,\Delta V\big], \text{etc.} \tag{D3}$$

while the area averages are represented by

$$\int_{\Delta A}\mathbf{t}_{(\mathbf{n})}\,dA = \langle\mathbf{t}_{(\mathbf{n})}\rangle\Delta A,\ \int_{\Delta A_x}\mathbf{t}_{(-\mathbf{i})}\,dA = \langle\mathbf{t}_{(-\mathbf{i})}\rangle\Delta A_x \text{ , etc.} \tag{D4}$$

It is our intention to examine Eq. (D2) in the limit as $\Delta V \to 0$, but before taking that limit, we need to use the *projected area theorem* in order to express the areas of the coordinate surfaces according to

$$\Delta A_x = (\mathbf{n}\cdot\mathbf{i})\Delta A \tag{D5a}$$

$$\Delta A_y = (\mathbf{n}\cdot\mathbf{j})\Delta A \tag{D5b}$$

$$\Delta A_z = (\mathbf{n}\cdot\mathbf{k})\Delta A \tag{D5c}$$

The projected area theorem is discussed by Stein and Barcellos (1992, Secs. 12.2 and 17.1). Equations (D5) can be used in Eq. (D2) to obtain a form containing only the oblique area, ΔA given by

$$\frac{d}{dt}\big[\langle\rho\,\mathbf{v}\rangle\,\Delta V\big] = \langle\rho\mathbf{b}\rangle\Delta V + \Delta A\Big[\langle\mathbf{t}_{(\mathbf{n})}\rangle + (\mathbf{n}\cdot\mathbf{i})\langle\mathbf{t}_{(-\mathbf{i})}\rangle + (\mathbf{n}\cdot\mathbf{j})\langle\mathbf{t}_{(-\mathbf{j})}\rangle + (\mathbf{n}\cdot\mathbf{k})\langle\mathbf{t}_{(-\mathbf{k})}\rangle\Big] \tag{D6}$$

We can eliminate the first two terms in this form of Euler's first law by recognizing that the volume, ΔV, tends to zero faster than the area, ΔA. To do this, we divide Eq. (D6) by ΔA and take the limit to obtain

$$\lim_{\Delta V\to 0}\left\{\frac{1}{\Delta A}\frac{d}{dt}\big[\langle\rho\,\mathbf{v}\rangle\,\Delta V\big]\right\} = \lim_{\Delta V\to 0}\left\{\langle\rho\mathbf{b}\rangle\frac{\Delta V}{\Delta A}\right\} + \lim_{\Delta V\to 0}\Big\{\langle\mathbf{t}_{(\mathbf{n})}\rangle + (\mathbf{n}\cdot\mathbf{i})\langle\mathbf{t}_{(-\mathbf{i})}\rangle + (\mathbf{n}\cdot\mathbf{j})\langle\mathbf{t}_{(-\mathbf{j})}\rangle + (\mathbf{n}\cdot\mathbf{k})\langle\mathbf{t}_{(-\mathbf{k})}\rangle\Big\} \tag{D7}$$

Given the limiting condition for the ratio of the volume to the area,

$$\lim_{\Delta V\to 0}\left(\frac{\Delta V}{\Delta A}\right) = 0 \tag{D8}$$

we see that the first two terms in Eq. (D7) tend to zero and we are left with a result involving only the four stress vectors acting on the tetrahedron illustrated in Fig. 1D.

$$0 = \mathbf{t}_{(\mathbf{n})} + (\mathbf{n}\cdot\mathbf{i})\mathbf{t}_{(-\mathbf{i})} + (\mathbf{n}\cdot\mathbf{j})\mathbf{t}_{(-\mathbf{j})} + (\mathbf{n}\cdot\mathbf{k})\mathbf{t}_{(-\mathbf{k})} \tag{D9}$$

On the basis of Cauchy's lemma, we have the following three relations

$$\mathbf{t}_{(-\mathbf{i})} = -\,\mathbf{t}_{(\mathbf{i})}\ ,\mathbf{t}_{(-\mathbf{j})} = -\,\mathbf{t}_{(\mathbf{j})}\ ,\mathbf{t}_{(-\mathbf{k})} = -\,\mathbf{t}_{(\mathbf{k})} \tag{D10}$$

which allow us to express Eq. (D9) in the form Cauchy's fundamental theorem:

$$\mathbf{t}_{(\mathbf{n})} = (\mathbf{n}\cdot\mathbf{i})\,\mathbf{t}_{(\mathbf{i})} + (\mathbf{n}\cdot\mathbf{j})\,\mathbf{t}_{(\mathbf{j})} + (\mathbf{n}\cdot\mathbf{k})\,\mathbf{t}_{(\mathbf{k})} \tag{D11}$$

This famous theorem specifies the *functional dependence* of the stress vector on the unit normal vector, **n**, and we need to use this result in Eqs. (27) and (28) in order to derive the governing point equations associated with Euler's two laws of mechanics. We begin with Eq. (D11) and rearrange that expression to obtain

$$\mathbf{t}_{(\mathbf{n})} = \mathbf{n}\cdot\big(\mathbf{i}\,\mathbf{t}_{(\mathbf{i})}\big) + \mathbf{n}\cdot\big(\mathbf{j}\,\mathbf{t}_{(\mathbf{j})}\big) + \mathbf{n}\cdot\big(\mathbf{k}\,\mathbf{t}_{(\mathbf{k})}\big) \tag{D12}$$

This encourages us to remove the unit normal vector as a common factor in order to express the stress vector as

$$\mathbf{t}_{(\mathbf{n})} = \mathbf{n}\cdot\Big[\big(\mathbf{i}\,\mathbf{t}_{(\mathbf{i})}\big) + \big(\mathbf{j}\,\mathbf{t}_{(\mathbf{j})}\big) + \big(\mathbf{k}\,\mathbf{t}_{(\mathbf{k})}\big)\Big] \tag{D13}$$

We now define the term in brackets is the stress *tensor*, $\mathbf{T}$, leading to the compact representation given by

$$\mathbf{t}_{(\mathbf{n})} = \mathbf{n}\cdot\mathbf{T} \tag{D14}$$

Here one can think of the stress tensor as *operating on* the vector **n** to produce the vector $\mathbf{t}_{(\mathbf{n})}$, or one can think of the stress tensor as *mapping* the vector **n** onto the vector $\mathbf{t}_{(\mathbf{n})}$.

Appendix E. Use of the chemical potential

In the development of the Stefan-Maxwell equations we made use of the ideal mixture relation given by

$$p_A = x_A\,p\ ,\ \textit{ideal mixture} \tag{E1}$$

and in this appendix we remove this limitation. We begin with the idea that the state of a system can be characterized by $N - 1$ mole fractions along with the temperature and pressure. To be explicit about this assumption we write

$$\left\{\begin{matrix}\text{state of an } N\text{-component}\\ \text{system}\end{matrix}\right\} = \mathscr{H}(x_A, x_B, x_C, ..., x_{N-1}, T, p) \tag{E2}$$

This representation does not apply to an elastic material for which the strain would also be required to specify the state, nor would it apply to a magnetic material for which the magnetic field would be required to specify the state. To be clear about dynamic systems, we note that the use of Eq. (E2) requires the assumption of *local thermodynamic equilibrium*. To give a specific example of this idea, it means that the functional dependence of the chemical potential of species A is taken to be (Prigogine and Defay, 1954, page 85)

$$\mu_A = \mu_A(x_A, x_B, x_C, ..., x_{N-1}, T, p) \tag{E3}$$

even in the presence of gradients such as ∇x_A, ∇T, and ∇p, or in the presence of time derivatives such as $\partial p \,/\, \partial t$, etc. This is a common assumption made in studies of transport phenomena, but it is rarely stated in a clear manner.

In this appendix we will avoid the limitation imposed by Eq. E1 and make use of the more general relation given by

$$p_A = f(x_A, x_B, x_C, ..., x_{N-1}, T, p)\,, \quad \textit{local thermodynamic equilibrium} \tag{E4}$$

In order to connect this development with that given in Sec. 2.6, it will be convenient to express the functional dependence of the partial pressure according to

$$p_A = x_A p + \mathscr{F}(x_A, x_B, x_C, ..., x_{N-1}, T, p) \tag{E5}$$

Furthermore, it will be convenient to express this in the general notation given by

$$p_A = x_A p + \mathscr{F}(\psi_A, \psi_B, \psi_C, ..., \psi_{N-1}, \psi_N, \psi_{N+1}) \tag{E6}$$

Use of this more general representation for the partial pressure in Eq. (131) leads to

$$\begin{aligned} &\frac{\partial}{\partial t}(\rho_A \mathbf{v}_A) + \nabla\cdot(\rho_A \mathbf{v}_A \mathbf{v}_A) - \rho_A \mathbf{b}_A + x_A \nabla p \\ &+ \sum_{B=1}^{B=N+1} \left(\partial\mathscr{F}/\partial\psi_B\right)\nabla\psi_B - \nabla\cdot\boldsymbol{\tau}_A - r_A \mathbf{v}_A \\ &= -p\nabla x_A + \sum_{B=1}^{B=N} \mathbf{P}_{AB}\,, \quad A = 1, 2, ..., N \end{aligned} \tag{E7}$$

and we can follow the development from Eq. (133) to Eq. (136) to obtain

$$\begin{aligned} &p^{-1}\left[\frac{\partial}{\partial t}(\rho_A \mathbf{v}_A) + \nabla\cdot(\rho_A \mathbf{v}_A \mathbf{v}_A) - \rho_A \mathbf{b}_A + x_A \nabla p \right.\\ &\left. - \nabla\cdot\boldsymbol{\tau}_A - r_A \mathbf{v}_A\right] + p^{-1}\sum_{B=1}^{B=N+1} \left(\partial\mathscr{F}/\partial\psi_B\right)\nabla\psi_B \\ &= -\nabla x_A + \sum_{B=1}^{B=N} \frac{x_A x_B(\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}}\,, \quad A = 1, 2, ..., N \end{aligned} \tag{E8}$$

At this point we represent the chemical potential as (Denbigh, 1955, page 269) as

$$\mu_A = \mu_A^{\mathrm{o}} + RT\ln(\gamma_A\, x_A)\,, \gamma_A \to 1 \text{ as } x_A \to 1 \tag{E9}$$

and form the gradient of the chemical potential to obtain

$$\begin{aligned} \nabla x_A = &\frac{x_A}{RT}\nabla\mu_A - \frac{x_A}{RT}\Big[\left(\partial\mu_A^{\mathrm{o}}/\partial T\right) + R\ln(\gamma_A\, x_A)\Big]\nabla T \\ &- \frac{x_A}{RT}\left(\partial\mu_A^{\mathrm{o}}/\partial p\right)\nabla p - x_A \nabla\ln(\gamma_A) \end{aligned} \tag{E10}$$

Substitution of this relation into Eq. (E9) leads to

$$\begin{aligned} &p^{-1}\left[\frac{\partial}{\partial t}(\rho_A \mathbf{v}_A) + \nabla\cdot(\rho_A \mathbf{v}_A \mathbf{v}_A) - \rho_A \mathbf{b}_A \right.\\ &\left. + x_A \nabla p - \nabla\cdot\boldsymbol{\tau}_A - r_A \mathbf{v}_A\right] \\ &+ p^{-1}\sum_{B=1}^{B=N+1} \left(\partial\mathscr{F}/\partial\psi_B\right)\nabla\psi_B \\ &- \frac{x_A}{RT}\Big[\left(\partial\mu_A^{\mathrm{o}}/\partial T\right) + R\ln(\gamma_A\, x_A)\Big]\nabla T \\ &- \frac{x_A}{RT}\left(\partial\mu_A^{\mathrm{o}}/\partial p\right)\nabla p - x_A \nabla\ln(\gamma_A) \\ &= -\frac{x_A}{RT}\nabla\mu_A + \sum_{B=1}^{B=N} \frac{x_A x_B(\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}}\,, \\ &\qquad A = 1, 2, ..., N \end{aligned} \tag{E11}$$

At this point we can follow Eqs. (150) through (152) to simplify this result to the form

$$\begin{aligned} &p^{-1}\rho_A(\mathbf{b} - \mathbf{b}_A) - p^{-1}(\omega_A - x_A)\nabla p \\ &+ p^{-1}\left(\omega_A \nabla\cdot\boldsymbol{\tau} - \nabla\cdot\boldsymbol{\tau}_A\right) \\ &+ p^{-1}\rho_A\left(\frac{\partial \mathbf{u}_A}{\partial t} + \mathbf{v}_A\cdot\nabla\mathbf{u}_A + \mathbf{u}_A\cdot\nabla\mathbf{v}\right) \\ &+ p^{-1}\sum_{B=1}^{B=N+1} \left(\partial\mathscr{F}/\partial\psi_B\right)\nabla\psi_B \\ &- \frac{x_A}{RT}\Big[\left(\partial\mu_A^{\mathrm{o}}/\partial T\right) + R\ln(\gamma_A\, x_A)\Big]\nabla T \\ &- \frac{x_A}{RT}\left(\partial\mu_A^{\mathrm{o}}/\partial p\right)\nabla p - x_A \nabla\ln(\gamma_A) \\ &= -\frac{x_A}{RT}\nabla\mu_A + \sum_{B=1}^{B=N} \frac{x_A x_B(\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}}\,, \\ &\qquad A = 1, 2, ..., N-1 \end{aligned} \tag{E12}$$

In some cases, all of the terms on the left hand side are discarded to obtain what is referred to as the generalized Stefan-Maxwell equations (Taylor and Krishna, 1993) given by

$$0 = -\frac{x_A}{RT}\nabla\mu_A + \sum_{B=1}^{B=N} \frac{x_A x_B(\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}}\,, \quad A = 1, 2, ..., N-1 \tag{E13}$$

Arguments are given in Sec. 2.7 suggesting that the *first four terms* on the left hand side of Eq. (E12) can often be discarded. The *fifth term* involves a series of corrections to the partial pressure for species A. The most important term in this series of terms would be the first one (for species A) that is given by $\left(\partial\mathscr{F}/\partial x_A\right)\nabla x_A$; however, there may be many situations in which this entire series of terms is negligible. It is plausible that the *sixth and seventh terms* are also negligible compared to either one of the two terms on the right hand side of Eq. (E12);

however, the *eighth term* is problematic. For ideal solutions, the Stefan-Maxwell equations represented by Eq. (146) should suffice. For non-ideal solutions, it is *difficult* to argue that

$$x_A \nabla \ln\left(\gamma_A\right) \ll \frac{x_A}{RT} \nabla \mu_A \tag{E14}$$

thus a more appropriate form of the generalized Stefan-Maxwell equations is given by

$$-x_A \nabla \ln\left(\gamma_A\right) = -\frac{x_A}{RT} \nabla \mu_A + \sum_{B=1}^{B=N} \frac{x_A x_B (\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}}, \quad A = 1, 2, \ldots, N-1 \tag{E15}$$

There are numerous variations of the basic Stefan-Maxwell equations to be found in the literature (Bird *et al*., 2002, page 769; Slattery, 1999, Sec. 8.4.4; Deen, 1998, Sec. 11.8); however, there would appear to be no detailed studies of the magnitude of the terms that are discarded or retained. On the basis of the material presented in Sec. 2.7 and the author's intuition, it would appear that Eq. (E15) should be the first choice if one wants to move beyond Eq. (146).