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The continuum mechanical theory of multicomponent diffusion in fluid mixtures

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ABSTRACT

The continuum mechanical approach for deriving the generalized equations of multicomponent diffusion in fluids is described here in detail, which is based on application of the principle of linear momentum balance to a species in a mixture, resulting in the complete set of diffusion driving forces. When combined with the usual constitutive equations including the continuum friction treatment of diffusion, the result is a very complete and clear exposition of multicomponent diffusion that unifies previous work and includes all of the various possible driving forces as well as the generalized Maxwell–Stefan form of the constitutive equations, with reciprocal diffusion coefficients resulting from Newton's third law applied to individual molecular encounters. This intuitively appealing and rigorous approach, first proposed over 50 years ago, has been virtually ignored in the chemical engineering literature, although it has a considerable following in the mechanical engineering literature, where the focus, naturally, has been physical properties of multiphase fluid and solid mixtures. The described approach has the advantages of transparency over the conventional approach of non-equilibrium thermodynamics and of simplicity over those based on statistical mechanical or kinetic theory of gases or liquids. We provide the general derivation along with some new results in order to call attention of chemical engineers to this comprehensive, attractive, and accessible theory of multicomponent diffusion in fluids.

1. Introduction

The theory of multicomponent diffusion and its various driving forces is treated in a large number of chemical engineering books and articles (of necessity, only representative publications are cited here), e.g., for: (1) fluids of different state of aggregation, i.e., in gaseous, liquid, electrolyte, polymer, and colloidal solutions (Bird et al., 2002; Curtiss and Bird, 1996, 1999; Cussler, 1976, 1997; Deen, 1998; Kerkhof and Geboers, 2005a, 2005b; Kuiken, 1994; Lightfoot, 1974; Newman, 1991; Slattery, 1981, 1999; Taylor and Krishna, 1993; Tyrrell and Harris, 1984; Wesselingh and Krishna, 1990); (2) porous media (Do, 1998; Jackson, 1977; Mason and Malinauskas, 1983; Mason et al., 1967; Whitaker, 1986, 1999); and (3) membranes (Datta et al., 1992; Mason and Lonsdale, 1990; Spiegler, 1958; Thampan et al., 2000). Although this general multicomponent diffusion theory is being increasingly utilized in the rigorous analysis of many chemical engineering mass transport problems (Amundson et al., 2003; Bird et al., 2002; Cussler, 1997; Datta and Rinker, 1985; Jackson, 1977; Krishna, 1987c; Krishna and Wesselingh, 1997; Lightfoot, 1974; Taylor and Krishna, 1993; Thampan et al., 2000; Wang and Datta, 1986), starting with the early work of Toor (1957) and Stewart and Prober (1964), its application is still somewhat limited. We feel that a reason for this is the lack of a clear exposition of the underlying principles of the multicomponent diffusion theory.

The conventional derivation of multicomponent diffusion in continua based on the non-equilibrium, or irreversible, thermodynamics, IRT (Bird et al., 2002; Curtiss and Bird, 1999; de Groot and Mazur, 1962) can be mystifying (Cussler, 1997), while that based on statistical mechanical or kinetic theory of gases (Hirschfelder et al., 1964) or liquids (Bearman and Kirkwood, 1958; Snell et al., 1967) can be intimidating and, thus, not generally discussed at length in the chemical engineering undergraduate or graduate curricula. As a result, the origin and the basis of the rather complex equations of multicomponent diffusion remain obscure to most chemical engineers. It is our purpose here, therefore, to provide their derivation based on the more transparent approach of species linear momentum conservation (Snell and Spangler, 1967; Truesdell, 1957, 1962), involving a balance of diffusion "drag" and diffusion "driving forces," and grounded in the familiar principles of the subject of continuum Transport Phenomena (Bird et al., 2002). Also provided are some clarifications and new results. The derivation provides very

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general results and without some of the approximations inherent in the other approaches.

The diffusive flux equations in multicomponent mixtures are typically written in two alternate forms, i.e., either in: (1) the generalized Fick–Onsager (GFO) form (Onsager, 1945), a generalization of Fick's law (Fick, 1855), in which the diffusive flux of a species i is written as a linear combination of the diffusion "driving forces" $\mathbf{d}_j$ for all species (Fitts, 1962) or in (2) the generalized Maxwell–Stefan form (GMS) (Lightfoot et al., 1962; Maxwell, 1866, 1868; Stefan, 1871) in which the diffusion driving force for the ith species $\mathbf{d}_i$ is written as a linear combination of the fluxes of all species. Owing to the assumed linearity between flux and driving forces, the GFO and the GMS forms are, in fact, interconvertible through the use of linear algebra (Bearman, 1959; Fitts, 1962). Alternatively, the continuum frictional approach (Laity, 1959; Lamm, 1957; Spiegler, 1958) provides expressions in the form of the GMS equations but involves frictional, or impedance, coefficients, ζ_{ij}, rather than the GMS binary diffusion coefficients, D_{ij}.

The generalized diffusion driving force for the ith species $\mathbf{d}_i$ comprises not only the usual composition gradient, but also thermal and pressure gradients, stresses, as well as external body forces. The usual approach to obtaining these different driving forces is that of non-equilibrium, or irreversible thermodynamics, i.e., IRT (de Groot, 1951; de Groot and Mazur, 1962; Eu, 1992; Fitts, 1962; Haase, 1969; Kuiken, 1994; Lightfoot, 1974; Merk, 1959; Yao, 1981); starting with the entropy balance (Jaumann, 1911), and incorporating in it the equations of mass, momentum, and energy balance. An inspection of the resulting entropy production term shows it to be a sum of the products of fluxes and driving forces, thus identifying the various diffusion driving forces contained in $\mathbf{d}_i$. The IRT approach furthermore utilizes the linearity postulate, i.e., that the flux of a species involves a linear combination of the driving forces of all species $\mathbf{d}_j$ (Bird et al., 2002). The results are applicable to any mixture, although the transport coefficients are treated as phenomenological coefficients satisfying certain symmetry, i.e., the Onsager reciprocal relations (ORR) (Monroe and Newman, 2006), and other constraints. A criticism of the IRT theory is provided by Truesdell and others (Truesdell, 1984), e.g., its assertion of a lack of coupling between mass and viscous dissipation fluxes and forces, owing to their different tensorial rank based on the postulate of Curie, and the seemingly arbitrary choice for the reference frame for flux.

The equations of multicomponent diffusion for gases, on the other hand, are derived based on the Chapman–Enskog approach (Chapman and Cowling, 1970; Eu, 1992; Ferziger and Kaper, 1972; Hirschfelder et al., 1964) to the solution of the Boltzmann equation, involving the assumption of linear deviations from the equilibrium Maxwell–Boltzmann distribution function for component i, in the form of a perturbation function, that provides both the different diffusion driving forces, i.e., concentration and pressure gradient and external forces, as well as the Maxwell–Stefan constitutive equation along with predictive expressions for the diffusion coefficients involved. The alternate approach for gases is the Grad–Zhdanov theory (Grad, 1949; Zhdanov et al., 1962), in which the distribution function for component i is written as a product of the equilibrium distribution function and a series of Hermite polynomials, and moments of the Boltzmann equation are generated for species i. The final result is modified expressions for the diffusion coefficients and the appearance of a stress term in the diffusion driving force that is absent in the Chapman–Enskog theory as well as in IRT. The Grad–Zhdanov theory also forms the starting point for the derivation of the Dusty-Gas Model (DGM) for gaseous transport in porous media (Cunningham and Williams, 1980; Mason et al., 1967; Kerkhof, 1996; Weber and Newman, 2005). The DGM has, unfortunately, also so far seen rather limited use in chemical engineering applications (Abed and Rinker, 1973; Datta et al., 1992; Datta and Rinker, 1985; Kaza and Jackson, 1980; Krishna, 1987b; Skrzypek et al., 1984; Suwanwarangkula et al., 2003; Thampan et al., 2001; Wang and Datta, 1986).

For the case of monatomic liquids, Bearman and Kirkwood (1958) derived the complete multicomponent diffusion equations in the form of partial momentum balance of species i from statistical mechanics of molecular dynamics based on the Liouville equation. They determined the perturbation in distribution functions due to departure from equilibrium and provided formal integral equations for transport coefficients. The Bearman–Kirkwood theory forms the starting point for the derivation of the Dusty-Fluid Model (DFM) for liquid transport in porous media and in membranes (Mason and Lonsdale, 1990; Mason and Viehland, 1978). The DFM has also seen only rather limited application so far (e.g., Noordman et al., 2002; Thampan et al., 2000; Syed and Datta, 2002). Curtiss and Bird (1996) have extended the Bearman–Kirkwood theory to polymeric liquids.

An alternate approach that has received scant attention in the chemical engineering literature, with few notable exceptions (Curtiss and Bird, 1996; Whitaker, 1986), although it is well-known in the mechanical engineering literature as the "Theory of Mixtures" (Bowen, 1976; Green and Naghdi, 1967) and applied to multiphase fluid and solid mixtures, is the theory of diffusion based on the linear momentum balance of species (Atkin and Craine, 1976b; Bowen, 1967; Müller, 1968; Snell and Spangler, 1967; Stefan, 1871; Truesdell, 1957, 1962, 1984; Truesdell and Toupin, 1960; Williams, 1958). This is unfortunate, since it provides a remarkably complete description of the various diffusion driving forces based on more readily understood continuum mechanical arguments. After all, diffusion involves relative "motion" of a species in response to driving "forces." It, therefore, stands to reason that a reliable description of diffusion should result from species linear momentum balance.

When combined with the "frictional drag" model, another well-accepted continuum mechanical model, it provides an inherently consistent and detailed description of multicomponent diffusion in fluid mixtures, involving both the various driving forces as well as the constitutive equations of the Maxwell–Stefan form. Of course, the transport coefficients are not predicted accurately by this elementary approach, for which one must resort to molecular theories (Reid et al., 1987) or experiments, although the right forms of expressions result (Furry, 1948; Maxwell, 1868; Ramshaw, 1993; Williams, 1958). Since the molecular theories (Hirschfelder et al., 1964; Kerkhof and Geboers, 2005a; Snell et al., 1967; Zhdanov et al., 1962) differ primarily in this regard, they are complementary, rather than competitors, to the continuum mechanical theory. Additionally, the constraints on the constitutive equations imposed by the Clausius–Duhem entropy inequality have been discussed at length in the mechanical engineering literature (Samohýl and Šilhavý, 1990). A limitation of a purely mechanical theory such as this is, of course, its inability to predict chemical mechanisms of diffusion. Thus, a notable exception is the Grotthuss mechanism (Choi et al., 2005; Grotthuss, 1806) for the anomalous proton diffusion, which, incidentally, predates Fick's law (Fick, 1855) by half a century!

The purpose of this paper, thus, is to provide a complete and self-contained derivation of the multicomponent diffusion equations based on the principle of linear species momentum balance along with the application of Newton's third law in an elementary treatment of frictional encounters among constituent molecules. This approach provides the most complete form of multicomponent diffusion equations available in the literature, derived normally via more esoteric means inaccessible to the nonspecialist, along with some additional new details. The simplicity of the approach and the underlying principle would hopefully encourage its further usage in chemical engineering education and research.