Physica A 389 (2010) 4026–4045

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Diffuse volume transport in fluids

Howard Brenner*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA

ARTICLE INFO

Article history:
Received 30 May 2010
Available online 13 June 2010

Keywords:
Transport processes
Volume
Diffusion
Constitutive equations
Irreversible thermodynamics

ABSTRACT

The diffuse flux of volume $\mathbf{j}_v$ in a single-component liquid or gas, the subject of this paper, is a purely molecular quantity defined as the difference between the flux of volume $\mathbf{n}_v$ and the convective flux of volume $\mathbf{n}_m\hat{v}$ carried by the flowing mass, with $\mathbf{n}_m$ the mass flux, $\hat{v} = 1/\rho$ the specific volume, and ρ the mass density. Elementary statistical–mechanical arguments are used to derive the linear constitutive equation $\mathbf{j}_v = D_S\nabla \ln \rho$, valid in near-equilibrium fluids from which body forces are absent. Here, D_S is the fluid's self-diffusion coefficient. The present derivation is based on Einstein's mesoscopic Brownian motion arguments, albeit applied here to volume- rather than particle-transport phenomena. In contrast to these mesoscale arguments, all prior derivations were based upon macroscale linear irreversible thermodynamic (LIT) arguments. D_S replaces the thermometric diffusivity α as the phenomenological coefficient appearing in earlier, *ad hoc*, derivations. The prior scheme based on α, which had been shown to accord with Burnett's well-known gas-kinetic constitutive data for the heat flux and viscous stress, carries over intact to now show comparable accord of D_S with these same data, since for gases the dimensionless Lewis number $\mathrm{Le} = \alpha/D_S$ is essentially unity. On the other hand for most liquids, where $\mathrm{Le} \gg 1$, use of D_S in place of α is shown to agree much better with existing experimental data for liquids. For the case of binary mixtures it is shown for the special case of isothermal, isobaric, force-free, Fick's law-type molecular diffusion processes that $\mathbf{j}_v = D\nabla \ln \rho$, where D is the binary diffusion coefficient. In contrast with the preceding use in the single-component case of both mesoscopic and LIT models to obtain a constitutive equation for $\mathbf{j}_v$, the corresponding mixture result is derived here without use of any physical model whatsoever. Rather, the derivation effectively requires little more than the respective definitions of the diffuse volume- and Fickian mass-fluxes.

1. Introduction

For the case of simple single-component fluids the standard listing [1] of those extensive fluid properties capable of undergoing transport, both convective and diffusive, consists of mass, linear (and angular) momentum, internal energy, and entropy. The term diffusive, as usual, refers to that portion of the total property flux driven by purely molecular agitation (Brownian motion) disassociated from the net movement of mass, with the diffuse flux of mass identically zero by definition.

Only recently has volume been added to this general list of properties [2] capable of being transported diffusively. However, because mass transport was already included in this prior list, the notion of volume transport was considered by many to be redundant. And, as a consequence, because of the belief that volume was incapable of being transported independently of that of mass, ergo, there can then be no diffusive transport of volume. Indeed, this is almost certainly the reason why volume transport had not been identified earlier as an independent physical property capable of being transported, not only convectively, but also diffusively. Explicitly, with $\mathrm{d}\mathbf{S} \cdot \mathbf{n}_m$ the mass flux across a directed element

---

* Tel.: +1 617 253 6687; fax: +1 617 258 8224.
E-mail address: hbrenner@mit.edu.

0378-4371/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physa.2010.06.010

of surface area d**S** fixed in space, the corresponding volume flux, $d\mathbf{S}\cdot\mathbf{n}_v$, has generally been believed to be given by the expression $\mathbf{n}_v = \hat{v}\mathbf{n}_m$, with $\hat{v} = 1/\rho$ the specific volume, wherein ρ is the mass density [2]. Were that true, the difference $\mathbf{n}_v - \hat{v}\mathbf{n}_m \overset{\text{def.}}{=} \mathbf{j}_v$, say, would be identically zero under all circumstances. This paper shows, *inter alia*, that the diffuse volume flux $\mathbf{j}_v$ is not generally zero for either single—or multicomponent fluids.

Were $\mathbf{j}_v = \mathbf{0}$, as commonly believed, the transport of volume would indeed not be independent of that of mass, whose transport through space obeys the continuity equation [1]

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{n}_m = 0. \tag{1.1}$$

That is, with $\rho = 1/\hat{v}$ and $\mathbf{n}_m = \mathbf{n}_v/\hat{v}$, Eq. (1.1) would morph into a form expressible solely in terms of the symbols $\hat{v}$ and $\mathbf{n}_v$, with the resulting expression, upon rearrangement, then being interpreted as the appropriate volume transport equation, namely

$$\left(\frac{\partial}{\partial t} + \mathbf{n}_v\cdot\nabla\right)\ln\hat{v} = \pi_v,$$

in which [2]

$$\pi_v = \nabla\cdot\mathbf{n}_v$$

is the temporal rate of production of volume per unit volume at a point of the fluid. (We do not assign identifying numbers to these latter two equations since they prove not to be physically correct, owing to their failure to include a diffuse flux of volume.)

Reasons for questioning the implicit claim of the redundancy of volume transport relative to that of mass are four-fold:

(i) Whereas mass is conserved, volume generally is not;

(ii) Whereas the diffusive flux of mass, say $\mathbf{j}_m$, is identically zero by definition, the corresponding diffuse flux of volume, say $\mathbf{j}_v$, the latter defined by the expression [2]

$$\mathbf{n}_v = \hat{v}\mathbf{n}_m + \mathbf{j}_v, \tag{1.2}$$

(in which the vector $\hat{v}\mathbf{n}_m$ represents the convective contribution to the volume flux) has not been formally proved to be zero as a consequence of the zero-valued diffuse mass flux;

(iii) The third reason pertains to the fact that whereas the diffuse mass flux $\mathbf{j}_m$ is, by definition, identically zero in all circumstances, including the case of mixtures, the corresponding diffuse volume flux $\mathbf{j}_v$ is, without doubt, not zero in the case of those mixtures whose partial specific volumes are different for each species in the mixture. (Discussion of this multicomponent situation, together with formal proof of the preceding statement, is postponed until later in the paper, namely in Section 5, so as not to distract from the present focus on single-component fluids.) Accordingly, the belief that the volume and mass fluxes are simply proportional to one another under any and all circumstances, namely that $\mathbf{n}_v = \hat{v}\mathbf{n}_m$, thus requiring that $\mathbf{j}_v = \mathbf{0}$ in accord with (1.2), is invalid in the case of mixtures whose species differ in their respective densities. Mixtures thus negate the prevailing view that volume cannot, in general, be transported independently of mass;

(iv) The fourth reason, one advanced by Dadzie, et al. [3] as a well as by Eu [4] is more subtle. It pertains to the statistical foundations of the kinetic theory of fluids, as embodied in the case of gases by the Boltzmann equation [5,6] and in the more general case, including liquids, by the general principles of statistical mechanics [4]. Explicitly, according to Dadzie, et al., fundamental questions regarding volume transport arise from the fact that with **x** the position of a molecule and with **v** its velocity, the usual probability density function $P_A(t, \mathbf{x}, \mathbf{v})$ is such that the quantity $P_A d\mathbf{x}\, d\mathbf{v}$ represents the probable number of molecules that, at time t, have their positions located within the physical-space volume element d**x** centered at **x** and their velocities within the elemental velocity-space domain d**v** centered at **v**. On the other hand, as pointed out by Dadzie, et al. [3], one can define a second probability density function $P_B(t, \mathbf{x}, \mathbf{v})$ for an arbitrary single molecule, such that $P_B d\mathbf{x} d\mathbf{v}$ represents the probability that, at time t, the velocity of this molecule lies within the differential velocity domain d**v** centered at **v** while the position of this single molecule lies within the volume element d**x** centered at **x**. Conventionally, it is supposed that $P_A = NP_B$ with N a fixed number of molecules. The quantity $\int P_A d\mathbf{v}$ is then interpreted as giving the average number of molecules per unit volume. However, Dadzie, et al. [3] note that these assertions presuppose that the summation over the one-particle distribution functions corresponding to each individual molecule furnishes the average number of molecules around a given position **x**. In turn, this implies, *inter alia*, that each molecule is statistically independent of its position relative to that of the others. Based upon this observation, those authors develop an effectively volume-based nonlocal kinetic theory, one that effectively incorporates into its formulation the relative positions of neighboring molecules. Readers interested in the consequences of their comments are referred to their original publications [3] (see also Ref. [4]). Suffice it to say here, *inter alia*, that according to their findings the notion of a nonzero diffuse volume flux in single-component fluids arises as an inevitable consequence of resolving the disparity between the two probability functions.