

ME 451C
Winter Quarter, 2004-05
Week # 5

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February 1, 2005

Abstract

Is the diffusion matrix $D_{\alpha\beta}$ unique? If not, how do we justify what everybody has been doing? How to remove the sloppiness in stating the Onsager Reciprocity Relation? Note that the kinetic theory derivation, or the “elementary” derivation, does not need the Onsager Reciprocity Relation. Read [1]. How about boundary conditions?

1 More on Duham-Gibb’s

In Week #4 Notes, the Duham-Gibb’s equation has evolved—with the help of the energy, momentum and species continuity equations—into eq.(21):

$$\rho T \frac{Ds}{Dt} = -\nabla \cdot \mathbf{q} + \bar{\tau} : \nabla \mathbf{V} + \sum_{\alpha=1}^N \mu_{\alpha} (\nabla \cdot \mathbf{j}_{\alpha}^* - W_{\alpha}). \quad (1)$$

We first divide through by T , and rewrite its left hand side with the help of the global continuity equation:

$$\frac{\partial(\rho s)}{\partial t} + \nabla \cdot (\mathbf{V} \rho s) = \frac{1}{T} \left(-\nabla \cdot \mathbf{q} + \bar{\tau} : \nabla \mathbf{V} + \sum_{\alpha=1}^N \mu_{\alpha} (\nabla \cdot \mathbf{j}_{\alpha}^* - W_{\alpha}) \right) \quad (2)$$

On the right hand side, we see two terms that involve the divergence operator. We manipulate them as follows:

$$\frac{1}{T} \left(-\nabla \cdot \mathbf{q} + \sum_{\alpha=1}^N \mu_{\alpha} \nabla \cdot \mathbf{j}_{\alpha}^* \right) = \nabla \cdot \left(-\frac{\mathbf{q}}{T} + \sum_{\alpha=1}^N \frac{\mu_{\alpha} \mathbf{j}_{\alpha}^*}{T} \right) \quad (3)$$

$$+ \mathbf{q} \cdot \nabla \frac{1}{T} - \sum_{\alpha=1}^N \mathbf{j}_{\alpha}^* \cdot \nabla \frac{\mu_{\alpha}}{T}. \quad (4)$$

We now rewrite Eq.(4) as follows:

$$\frac{\partial(\rho s)}{\partial t} = \nabla \cdot \left(-\frac{\mathbf{q}}{T} + \sum_{\alpha=1}^N \frac{\mu_{\alpha} \mathbf{j}_{\alpha}^*}{T} - \mathbf{v} \rho s \right) + \left(\dot{\zeta}^* + \frac{\bar{\tau} : \nabla \mathbf{V}}{T} - \sum_{\alpha=1}^N \mu_{\alpha} W_{\alpha} \right) \quad (5)$$

where $\dot{\zeta}^*$ is short-hand for all diffusion-related terms:

$$\dot{\zeta}^* = \mathbf{q} \cdot \nabla \frac{1}{T} - \sum_{\alpha=1}^N \mathbf{j}_{\alpha}^* \cdot \nabla \frac{\mu_{\alpha}}{T} \quad (6)$$

$$= -\left(\mathbf{q} - \sum_{\alpha=1}^N \mu_{\alpha} \mathbf{j}_{\alpha}^* \right) \cdot \frac{\nabla T}{T^2} - \sum_{\alpha=1}^N \mathbf{j}_{\alpha}^* \cdot \frac{\nabla \mu_{\alpha}}{T}. \quad (7)$$

The left hand side of Eq.(5) is the rate of change of entropy in a small fixed volume. The right hand side of Eq.(5) says this change can come from two reasons. The first (divergence) term represents the impact of *fluxes* through the surface of the small volume, and the second bracketed term represents the impact of three possible *volume sources* inside the fixed volume—diffusion, viscosity (we are familiar with this term in single component fluid mechanics) and chemical reactions.

The $\dot{\zeta}^*$ term is what we are interested in. The Second Law of Thermodynamics says $\dot{\zeta}^*$ must be non-negative.

1.1 Independence of the \mathbf{j}_{α}^* 's

Since, by definition, the \mathbf{j}_{α}^* 's are not independent. They must honor:

$$\sum_{\alpha=1}^N \mathbf{j}_{\alpha}^* = 0. \quad (8)$$

Consequently, the following are always true:

$$\sum_{\alpha=1}^N \mu_{\alpha} \mathbf{j}_{\alpha}^* = \sum_{\alpha=1}^N (\mu_{\alpha} - \mu_{\beta}) \mathbf{j}_{\alpha}^*, \quad (9)$$

$$\sum_{\alpha=1}^N \mathbf{j}_\alpha^* \cdot \frac{\nabla \mu_\alpha}{T} = \sum_{\alpha=1}^N \mathbf{j}_\alpha^* \cdot \frac{\nabla(\mu_\alpha - \mu_\beta)}{T} \quad (10)$$

for any $1 \leq \beta \leq N$.¹ Without loss of generality, we shall set $\beta = N$.² Thus Eq.(7) can be rewritten as follows:

$$\dot{\zeta}^* = -\left(\mathbf{q} - \sum_{\alpha=1}^{N-1} \tilde{\mu}_\alpha \mathbf{j}_\alpha^*\right) \cdot \frac{\nabla T}{T^2} - \sum_{\alpha=1}^{N-1} \mathbf{j}_\alpha^* \cdot \frac{\nabla \tilde{\mu}_\alpha}{T}, \quad (11)$$

where

$$\tilde{\mu}_\alpha \equiv \mu_\alpha - \mu_N. \quad (12)$$

1.2 Conjugated Fluxes and Affinities

In the Onsager literature, Eq.(11) is said to contain N *fluxes* \mathbf{F}_n :

$$\mathbf{F}_n = \mathbf{j}_1^*, \dots, \mathbf{j}_{N-1}^*, \mathbf{q} - \sum_{\alpha=1}^{N-1} \tilde{\mu}_\alpha \mathbf{j}_\alpha^*, \quad (13)$$

and N “affinities” \mathbf{X}_n :

$$\mathbf{X}_n = \frac{\nabla \tilde{\mu}_1}{T}, \dots, \frac{\nabla \tilde{\mu}_{N-1}}{T}, \frac{\nabla T}{T^2}. \quad (14)$$

Note that \mathbf{F}_N and \mathbf{X}_N have different physical dimensions from their respective cohorts. In terms of them, Eq.(11) can be rewritten in the following pretty form:

$$\dot{\zeta}^* = - \sum_{n=1}^N \mathbf{F}_n \mathbf{X}_n. \quad (15)$$

These fluxes and these affinities are said to be *conjugates* to each other. Most importantly, the N components of \mathbf{F}_n are independent entities, and so are the N components of \mathbf{X}_n —and Eq.(8) is always honored. Now, the theoretical question is: how are the \mathbf{F}_n ’s related to the \mathbf{X}_n ’s?

¹In class, I emphasized that one may choose anything—so long as it is independent of α —to play the role of μ_β .

²There is actually a caveat. To be totally honest and above board, species N should be a “majority” species; it must not be a “trace” species. The choice of $\beta = N$ is only to provide simpler notations in the summations.

1.3 Linear Constitutive Relation

Obviously, if all the affinities (spatial gradients) were zeros, there would be no fluxes. So the simplest (linear) constitutive relation between them would be:

$$\mathbf{F}_n = - \sum_{m=1}^N L_{nm} \mathbf{X}_m, \quad (16)$$

where L_{nm} is a $N \times N$ real matrix. All of its $N \times N$ components are functions of the state variables ($p, \rho, T, Y_\alpha, \dots$).

Here is where Onsager's Reciprocity Relation comes in. It says L_{nm} is symmetric. So instead of needing N^2 numbers to represent this matrix, we only need $N(N + 1)/2$ numbers. When N is a big integer, this is very helpful.

The Onsager Reciprocity Relation is a theoretical prediction from statistical mechanics. It has ample experimental verifications. It cannot be deduced from the Second Law of Thermodynamics or any macroscopic, phenomenological rationalizations. You have access to the two original Onsager papers. I am unable to say that I can follow the derivations presented.

1.4 Soret and Dufour

The elements $L_{\alpha N}$ represents mass fluxes induced by temperature gradient—it is called the *Soret* effect. The elements $L_{N\alpha}$ represents heat flux induced by chemical potential gradients—it is called the *Dufour* effect. The Onsager Reciprocity Relation says $L_{N\alpha} = L_{\alpha N}$.

1.5 Consistency Check

To take k items from N available items, the number of permutations is $N!/(N - k)!$, and the number of combination is $N!/(k!(N - k)!)$.

Given N species, there are $N(N - 1)/2$ binary collision types. So there are $N(N - 1)/2$ binary (momentum exchange) collisional frequencies ($\bar{m}_{\alpha\beta}\nu_{\alpha\beta}$'s in Week # 4 Notes).

If we consider the $(N - 1)$ independent mass fluxes which are properly conjugated with the $(N - 1)$ independent $\tilde{\mu}_n$ gradients, we have a $(N - 1) \times (N - 1)$ mass diffusion coefficient matrix. Since this matrix is symmetric, the number of independent elements is— $[(N - 1)^2 - (N - 1)]/2$ off-diagonal elements and $[N - 1]$ diagonal

elements— $N(N - 1)/2$, the same number as the number of binary collision types. So this is a consistency check.

2 A less sloppy statement of Onsager’s Reciprocity Relation

The following is a list of common sloppiness in the Onsager literature:

1. \mathbf{F}_n and \mathbf{X}_n are not properly conjugated. The one-sentence indictment by Coleman and Truesdell is irrefutable (see reference [7] in Week #4 Notes).
2. The components of \mathbf{F}_n are not independent—as would be the case before enforcing Eq.(8) by the μ_β trick.

Thus, a less sloppy statement of the Onsager Reciprocity Relation is:

The square non-singular³ matrix which relates properly (in accordance with $\dot{\zeta}^*$) conjugated fluxes and affinities—each consists of independent components—is symmetric.

It is useful to note that the Onsager Reciprocity Relation does not guarantee the non-negativity of $\dot{\zeta}^*$. This requirement only imposes conditions on the signs and certain inequalities of the elements of the symmetric $L_{nn'}$.

It is emphasized that the diffusion matrix is non-unique until it is made unique by imposing Eq.(8) somehow. This issue made its presence felt in the “elementary” derivation. However, it is seldom stated clearly in the literature. But if you look carefully, one or more of the majority species is often ignored.

3 Commonly adopted approximations

When diffusion is an important aspect of a N -component fluid mechanics problem, it is often the case that all not N species are of interest. If less than N species are being tracked, then Eq.(8) can be assumed to be honored by the ignored species. Very frequently, the matrix $D_{\alpha\beta}$ for the interested species is taken to be diagonal (thus symmetric), and the diffusion coefficients would be approximated by some “mixture rules” of binary diffusivities (*e.g.* Blanc’s (empirical)

³If this matrix is singular, then it is non-unique. Ask me in class if this is not clear.

Law). Once a diagonal $D_{\alpha\beta}$ is adopted, the coupling *between* species comes from the composition-dependence of the diagonal elements *and* the chemistry term W_α . If there is no chemistry term, the coupling is weak. If there is an active chemistry term, it is a different story (we will get into this later).

It is interesting that the chemical potential, μ_α , plays a central role in the classical continuum theories of diffusion, while in the kinetic (and the “elementary”) theories, it makes no appearance at all.

4 Boundary conditions

Once a diffusion law is adopted, the PDE governing the mass fraction, Y_α , is a diffusion equation. Loosely speaking, it needs initial condition, and boundary conditions. We need to talk about boundary condition at a solid-fluid interface.

Boundary condition comes from the physics of the problem. What happens at a solid surface? A molecule of the α species strikes the solid wall, and something bounces off the wall. The net mass flux to a solid wall is the normal component of \mathbf{j}_α^* at the wall.

If the wall is not *catalytic*—no chemistry happens at the wall surface—then the boundary condition is the normal component of \mathbf{j}_α^* be zero at the wall.

Now what happens if the wall is catalytic? Consider first the ideal catalytic wall when *every* α molecule striking it got married on the surface, and bounces off as species $\alpha + 1$? (For example, species α is CO and species $\alpha + 1$ is CO_2 ; or species α is a positively charged ion, and species $\alpha + 1$ is a neutral particle). What would then be a reasonable estimate of the mass averaged velocity (\mathbf{v}_α^*) of the α molecules approximately one mean-free-path away from the catalytic surface?

The rest of this discourse will be left as a homework problem.

5 Something to ponder on

What happens when there is chemical reaction? How does chemical reaction and diffusion (molecular or turbulent) interact?

6 Homeworks

1. Suppose someone comes up with a $L_{nn'}$ matrix to relate the fluxes and the affinities. You check up on the matrix, and found that the set of eigenvalues of this matrix includes a zero eigenvalue. What can you say about the linear independence of the fluxes?
2. In the “elementary derivation” presented in Week # 4 Notes, we put $\rho_\alpha \mathbf{h}_\alpha$ in eq.(22), the species specific momentum equation. We said it represented all other complications not so far included or properly accounted for. Then we defined \mathbf{h} by eq.(39).

Now suppose we explore the theoretical consequence of the following hypothesis:

$$\mathbf{h}_\alpha = K_\alpha \nabla T \quad (17)$$

where K_α honors:

$$\sum_{\alpha=1}^N Y_\alpha K_\alpha = 0 \quad (18)$$

so that $\mathbf{h} = 0$. Compare eq.(41) and eq.(3) of Week # 4 Notes. Find the relation between $D_\alpha^{(T)}$ and K_α and whatever other parameters that may be involved.⁴

3. Look at eq.(3) of Week # 3 Notes. What is the physical dimension of $D_{\alpha\beta}$? Suppose you guess that it should depend on the average random (colliding) velocity of the α molecules and their average mean-free-path. Can you give an intelligent formula relating them? Now comes the interesting question: what would you use for boundary condition for the α species (either X_α or Y_α) at a catalytic surface? If you do not have an ideal catalytic surface, but only one α molecules out of ten arriving on the surface got married when they bounce off. How much does the performance of the catalytic surface degrade (under “normal” conditions)?

⁴A plausible physical explanation of $D_\alpha^{(T)}$ is that the “effective cross-section” of momentum exchange collisions is temperature dependent (unlike hard spheres).

References

- [1] Landau and Lifshitz, Fluid Mechanics, Vol. 6 (Course of Theoretical Physics), §58-59, Butterworth-Heinemann; 2nd Edition, 1987.