A New Continuum Formulation for Materials–Part I. The Equations of Motion for a Single-Component Fluid

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Abstract

The continuum equations of fluid mechanics are rederived with the intention of keeping certain mechanical and thermodynamic concepts separate. A new "mechanical" mass density is created to be used in computing inertial quantities, whereas the actual mass density is treated as a thermodynamic variable. A new set of balance laws is proposed, including a mass balance equation with a non-convective flux. The basic principles of irreversible thermodynamics are used to obtain linear constitutive equations that are expansions of not only the usual affinities involving gradients of temperature and velocity–but also the gradient of the chemical potential. Transport coefficients are then chosen based on an elementary diffusion model, which yields simple constitutive laws featuring just one diffusion transport parameter. The resulting formulation differs from the Navier-Stokes-Fourier equations of fluid motion. In order to highlight key similarities and differences between the two formulations, several fluid mechanics problems are examined, including sound propagation, light scattering, steady-state shock waves, and thermophoresis.

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1 Introduction

The starting point for the theory proposed here is simple but somewhat abstract. Instead of the five equations and five unknowns that the Navier-Stokes-Fourier formulation employs to describe a single-component fluid in three spatial dimensions, this formulation requires six (although the number of equations/unknowns drops back down to five for the linearized problem). The extra equation governs a new quantity, which I call the mechanical mass density and label as \( \bar{m} \). It is a book-keeping variable to be used when defining inertial quantities such as linear and angular momentum and kinetic energy.

The mechanical mass density is assumed to satisfy a continuity equation with nothing but convection to move it, while the (actual) mass density \( m \) is governed by a balance law that includes a mass diffusion term in addition to a convection term.

Behind the equations of motion that follow, a philosophy has been adopted to keep thermodynamics and mechanics separate in some key respects. The non-convective mass flux, \( \bar{q}_{M} \), is treated as one would the non-convective heat or internal energy flux, not, in other words, as a momentum involving a diffusion velocity. It is assumed to be dissipative and, consequently, its form is chosen based on non-equilibrium thermodynamic principles. On the other hand, the mechanical mass density may be viewed as the background mass density the material would have if it were somehow in a state of thermodynamic equilibrium with only the velocity field directly affecting it through the laws of continuum mechanics. The balance laws stemming from these ideas are proposed in §3. In them, there appears a local continuum mechanical velocity, \( \bar{v} \), which is used in the convection terms and in the definitions of the momentum and kinetic energy densities. Also, in these inertial density definitions, the mechanical mass density is employed instead of the actual mass density. Finally, when postulating a form for the total pressure tensor appearing in the momentum equation, there is no allowance for mass diffusion effects, nor are mass diffusion and external body forces allowed to affect one another directly.

The above statements warrant clarification: I am not claiming there to be an absence of inertial effects arising from the mass diffusion. After all, one may define momentum and kinetic energy densities involving the actual mass density or the total mass flux and then postulate balance laws for the time rate of change of those quantities. I prefer not to work with these, however, as their balance
laws are complicated by cross-effects. Within my formulation, the velocity \( v \) is not responsible for the overall mass flow. Instead, it is seen to govern, through convection, only the mechanical part of the flow, e.g. that which is caused by pressure disturbances, moving boundaries, gravity, etc., whereas the diffusional part of the mass flow is handled separately in accordance with non-equilibrium thermodynamics. With this in mind, the balance laws given in §3 for the linear momentum, angular momentum, and kinetic energy densities are understood to be laws for the mechanical part of the linear momentum, angular momentum, and kinetic energy densities. There are some interesting benefits to this approach. (1) It circumvents the angular momentum conservation issues and other concerns raised in Öttinger et al. [35], (2) because the diffusional part of the mass flux can be made to cancel with the convective part, it allows us to model an impermeable boundary with a non-zero normal velocity at that boundary—see §7.3.1 as arising in the case of non-infinite acoustic impedance at a sound barrier—see Morse and Ingard [33], and (3) after appropriate constitutive equations and transport coefficients are chosen, it leads to the case of pure diffusion via Fick’s law when mass density gradients are present yet conditions have been chosen to eliminate all mechanical forces—see §7.2.

In §4 and Appendix C, the principles of irreversible thermodynamics are used to select general forms for the dissipative fluxes appearing in the balance laws. The Navier-Stokes-Fourier formulation possesses two dissipative fluxes, the heat flux and the viscous pressure tensor, whereas mine at the outset possesses four: the aforementioned two, plus a non-convective mass flux and an energy flux due to chemical work. Expressions for the chemical energy and heat fluxes are chosen in strict analogy to the first law of equilibrium thermodynamics.\(^1\) With standard techniques, my formulation produces linear constitutive laws that are expanded in terms of the usual affinities involving gradients of the velocity and temperature, as in the case of the Navier-Stokes-Fourier formulation. However, there arise additional terms involving gradients of the chemical potential. Since the non-convective internal energy flux may be expressed as the sum of those due to heat and chemical work, my formulation is found to have three independent constitutive laws and six transport coefficients (two for each law), five of which are independent if Onsager reciprocity is enforced.\(^2\) It may be difficult, if not impossible, to devise experiments for measuring each of my general transport coefficients individually. Therefore, the proposed framework would not be very convenient or useful without a transport model to guide specific choices for the formulas of these transport coefficients.

Many thermodynamics textbooks, e.g. Reif [37, Ch.12], present a simple particle diffusion model as an introduction to non-equilibrium transport pro-

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1This may be a bit of an unusual idea in itself as, for mixtures anyway, it is common practice to construct a generalized heat flux by lumping chemical work terms in with the heat. See, for example, de Groot and Mazur [10, ch.III, §3].

2It should be noted that at this stage, one could choose the coefficients in my formulation such that the non-convective mass flux vanishes, thereby yielding the Navier-Stokes-Fourier formulation as a special case, with its two constitutive laws and three transport parameters (bulk and shear viscosity and heat conductivity).
cesses, the general idea being that the particles of a gas diffuse via random collisions with one another, and they carry with them extensive quantities, such as momentum and energy, which are exchanged during the collisions. These types of models, constructed for a classical monatomic ideal gas, are found to be qualitatively useful but quantitatively inaccurate, and thus they are immediately discarded for more complicated procedures based on the Boltzmann equation. However, within the setting of my general formulation, it is of interest to revisit these ideas of particle diffusion. I claim that my construction makes such an elementary picture a viable way of describing non-equilibrium transport in fluids.

Moreover, the ideas behind this model are not constrained to the very restrictive case of a classical monatomic ideal gas. In §5 a transport model is proposed in which diffusing groups of particles have random encounters with other groups, whereby they exchange not only momentum and energy, but also mass. This gives rise to formulas for all six transport coefficients involving just one diffusion parameter, $D$. Furthermore, Onsager reciprocity and the second law of thermodynamics are both automatically satisfied, the latter requiring only that the fluid have intrinsic equilibrium thermodynamic stability and $D \geq 0$. The heat flux law arising from such a model turns out to be different from Fourier’s, and the diffusion transport assumption results in a new form for the viscous pressure, as well. Of course, it is important to be able relate $D$ to the typical transport parameters, the bulk and shear viscosities and heat conductivity, in problems for which the Navier-Stokes-Fourier formulation is known to give the right answer. This is easily done by using sound attenuation data, for example, as shown in §7.3. An equally important issue is that there must be a way of experimentally distinguishing between the two theories for a problem where the Navier-Stokes-Fourier equations can be shown to fail. Light scattering, addressed in §7.5, may prove to be such an experiment, and it is currently being conducted.

When considering the dimensionless Knudsen number, $Kn$, defined as the ratio of the fluid’s mean free path length to some characteristic length scale in a particular problem, it should be emphasized that, like Navier-Stokes-Fourier, mine is a formulation intended to be used in the hydrodynamic, or small $Kn$, regime. I do not make any general claims that my continuum formulation works well into the more rarefied gas regime, although experimental data for sound propagation in the noble gases shows that mine performs significantly better than Navier-Stokes-Fourier there—see Figure 1. The previously mentioned light scattering experiment is being designed to study gases fully in the hydrodynamic regime which, up until now, has either been ignored or not adequately resolved in all other such experiments.

Sound propagation, light scattering, and several other problems are explored in §7. As a general rule, one finds that the formulas derived from my equations tend to be, in many ways, much simpler and easier to interpret than those obtained from the Navier-Stokes-Fourier theory. In fact for some problems, when

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3 Although the simplest version uses only one $D$, there is a little bit of flexibility regarding this issue as discussed in Appendix D.
only approximate answers may be computed with the Navier-Stokes-Fourier equations, exact solutions result from my theory. Another convenience is that, as demonstrated in Appendix F it is quite easy to obtain values for the diffusion parameter $D$, especially when compared to the task of measuring the three transport parameters required for the Navier-Stokes-Fourier formulation.

Despite these appealing features, there are two aspects of my formulation that may appear troubling. (1) The mechanical mass density is not a directly measurable quantity, and (2) my formulation is incompatible with the kinetic theory of gases. Regarding the first item, it should be observed that there are many instances of well-accepted macroscopic theories that involve computationally useful, but not directly measurable, quantities. The admitted difference here is that one is accustomed to conceiving of the mass density as an absolute concept with no ambiguity built into its definition and, therefore, seeming to present no need for alternate definitions. It is typical for more licence to be granted when defining new velocities and energies, for example. Although the mechanical mass density is an abstract concept, my theory uses it not in place of—but rather in conjunction with—the actual mass density, which is a quantity that is measurable and tied, in an averaged sense, to the masses of the molecules comprising the fluid. The second of the concerns mentioned above carries more significance. The incompatibility is evident from the fact that the Navier-Stokes-Fourier equations may be derived from the Boltzmann equation via the Chapman-Enskog procedure for the special case of a classical monatomic ideal gas (see Huang [21, Ch.6], for example). With this procedure, the Navier-Stokes-Fourier formulation is the first-order approximation in the parameter $Kn$. It must be emphasized that the difference between Navier-Stokes-Fourier and my theory is not a higher-order $Kn$ effect. Therefore, mine may not be developed from the Burnett equations or Grad’s moment method, for example. The connection between Navier-Stokes-Fourier and kinetic gas theory is generally interpreted to mean that both are correct, but perhaps both are missing the same concept. I realize that without proof, this seems like a heretical claim. However, if the results of the aforementioned light scattering experiment support my theory, then this would necessitate a reconception of kinetic gas theory in the hydrodynamic regime.

I have not been alone in my efforts to include an extra diffusive mechanism as part of the fluid equations of motion. For early examples, see Slezkin [39, 40] and Vallander [43], and for later examples, see Klimontovich [26, 27], Brenner [3, 4, 6, 8], and Dadzie et al. [14]. My formulation proves to be significantly different from each of these treatments.

\[\text{The physical idea of an impenetrable surface, for example, requires that no actual mass may go through the surface, whereas this condition does not, in itself, bar mechanical mass from going through the surface.}\]
2 Notation

To facilitate the subsequent development, let us first mention a few notational items. The number of lines under a symbol indicates its tensor order: a scalar (zeroth-order tensor) has no underlines (e.g. temperature, $T$), a first-order tensor has one underline (e.g. velocity, $v$), a second-order tensor has two underlines (e.g. pressure tensor, $P$), etc. A tensor of arbitrary order is indicated in bold. The symbol $1$ is used to represent the second-order identity tensor and $\mathbf{0}$ and $\mathbf{0}$ to denote the zero vector and zero second-order tensor, respectively. All of the tensor operators used in this paper are defined in Appendix A.

Extensive quantities, i.e. ones that are additive over composite subsystems, are denoted using capital letters. Below is a list of the extensive quantities considered here.

$$
\overline{M} = \text{mechanical mass} \quad L = \text{angular momentum} \quad W = \text{potential energy} \\
M = \text{mass} \quad E = \text{total energy} \quad S = \text{entropy} \\
V = \text{volume} \quad U = \text{internal energy} \\
P = \text{linear momentum} \quad K = \text{kinetic energy}
$$

The densities (amounts per volume) corresponding to the extensive quantities above are denoted using lower-case letters. For example, $l$ is the angular momentum density, $m$ is the mechanical mass density, etc. For any extensive quantity, $A$, its amount per unit mechanical mass is denoted as $a\left(\overline{M}\right)$. For example, $u\left(\overline{M}\right)$ is the internal energy per mechanical mass. Note that

$$u\left(\overline{M}\right) = \frac{1}{\overline{m}} \quad \text{(1)}$$

and

$$a = \overline{m} a\left(\overline{M}\right). \quad \text{(2)}$$

The intensive quantities considered in this paper are

$T = \text{absolute temperature}$$
$P = \text{thermodynamic pressure}$$
$\mu = \text{chemical potential (per mass)},$

and the remaining symbols to be defined are

$p = \text{position}$
$t = \text{time}$
$v = \text{continuum mechanical velocity}$

and a few others that are defined as they arise in the text and listed in Appendix G.

3 Balance Laws

The general balance law for an extensive quantity, $A$, is given by

$$\frac{\partial a}{\partial t} = -\nabla \cdot j_A + r_A, \quad \text{(3)}$$
where \( \mathbf{a} \) is the local \( \mathbf{A} \)-density which is assumed to depend on \( \mathbf{x} \) and \( t \), \( \mathbf{j}_\mathbf{A} \) is the total \( \mathbf{A} \)-flux, and \( \mathbf{r}_\mathbf{A} \) denotes the volumetric \( \mathbf{A} \)-production/destruction rate. Let us decompose the total flux into its non-convective and convective parts:

\[
\mathbf{j}_\mathbf{A} = \mathbf{q}_\mathbf{A} + \mathbf{v}_\mathbf{A}.
\]  \( \text{(4)} \)

In my proposed continuum formulation for a single-component fluid, I begin by assuming the local balance laws for the mechanical mass, mass, moment, total energy, and entropy to be given respectively by

\[
\frac{\partial \bar{m}}{\partial t} = -\nabla \cdot (\bar{m} \mathbf{v}) \quad \text{(5)}
\]

\[
\frac{\partial m}{\partial t} = -\nabla \cdot \left( \mathbf{q}_M + m \mathbf{v} \right) \quad \text{(6)}
\]

\[
\frac{\partial (\bar{m} \mathbf{v})}{\partial t} = -\nabla \cdot \left( \mathbf{P} + \bar{m} \mathbf{v} \mathbf{v} \right) + \bar{m} f^{(\mathbf{M})} \quad \text{(7)}
\]

\[
\frac{\partial e}{\partial t} = -\nabla \cdot \left( \mathbf{q}_{\text{heat}} + \mathbf{q}_{\text{chem}} + \mathbf{P} \cdot \mathbf{v} + e \mathbf{v} \right) \quad \text{(8)}
\]

and

\[
\frac{\partial s}{\partial t} = -\nabla \cdot \left( \mathbf{q}_s + s \mathbf{v} \right) + \mathbf{r}_s. \quad \text{(9)}
\]

Note that equation (5) is a continuity equation for the mechanical mass density and that equation (6) governing the actual mass density contains an additional non-convective mass flux. In momentum equation (7), the momentum density is assumed to be

\[
\mathbf{p} = \bar{m} \mathbf{v} \quad \text{(10)}
\]

Also, \( \mathbf{P} \) denotes the total pressure tensor, i.e. the non-convective momentum flux, \( \mathbf{q}_M \), and \( f^{(\mathbf{M})} \) is defined to be the external body force per mechanical mass, assumed conservative, which in this setting means to satisfy

\[
f^{(\mathbf{M})} = -\nabla w^{(\mathbf{M})} \quad \text{(11)}
\]

with

\[
\frac{\partial w^{(\mathbf{M})}}{\partial t} = 0. \quad \text{(12)}
\]

In the total energy equation (8), there appear, as usual, the heat flux, \( \mathbf{q}_{\text{heat}} \), and the energy flux arising from mechanical work, \( \mathbf{P} \cdot \mathbf{v} \), but I have also included an energy flux due to chemical work, \( \mathbf{q}_{\text{chem}} \).

Based on equations (5)-(9), there are a few others which may be derived. Defining the kinetic energy density as

\[
k = \frac{1}{2} \bar{m} \| \mathbf{v} \|^2, \quad \text{(13)}
\]
it is shown in Appendix B that equations (5) and (7) may be used along with
a few tensor identities to compute the following kinetic energy balance law:
\[
\frac{\partial k}{\partial t} = -\nabla \cdot \left( \mathbb{P} \cdot \mathbb{v} + k \mathbb{u} \right) + \mathbb{P}^T : \nabla \mathbb{u} + \mathbb{m} \mathbb{v} \cdot f^{(\mathbb{M})},
\]
(14)
or using (11) in the last term,
\[
\frac{\partial k}{\partial t} = -\nabla \cdot \left( \mathbb{P} \cdot \mathbb{v} + k \mathbb{u} \right) + \mathbb{P}^T : \nabla \mathbb{v} - \mathbb{m} \mathbb{v} \cdot \nabla w^{(\mathbb{M})}.
\]
(15)
Also, since (2) implies that the potential energy density may be expressed as
\[
w = \mathbb{m} w^{(\mathbb{M})},
\]
(16)
one may employ (5) and assumption (12), to obtain the following equation for
the potential energy:
\[
\frac{\partial w}{\partial t} = -w^{(\mathbb{M})} \nabla \cdot (\mathbb{m} \mathbb{v}).
\]
(17)
Therefore, by defining the internal energy density, \( u \), via
\[
e = u + k + w,
\]
(18)
one finds that (8), (15), and (17), together with identity (254), yield the internal
energy balance law,
\[
\frac{\partial u}{\partial t} = -\nabla \cdot \left( \mathbb{q}_{\text{heat}} + \mathbb{q}_{\text{chem}} + \mathbb{m} \mathbb{v} \right) - \mathbb{P}^T : \nabla \mathbb{v}.
\]
(19)
In view of the above, the non-convective internal energy flux is given by
\[
\mathbb{q}_{\text{U}} = \mathbb{q}_{\text{heat}} + \mathbb{q}_{\text{chem}}.
\]
(20)
Next, let us define the angular momentum density to be
\[
\mathbb{l} = \mathbb{x} \times \mathbb{m} \mathbb{v}
\]
(21)
and use (7) to compute the angular momentum balance as
\[
\frac{\partial \left( \mathbb{x} \times \mathbb{m} \mathbb{v} \right)}{\partial t} = \mathbb{x} \times \frac{\partial \mathbb{m} \mathbb{v}}{\partial t}
\]
\[
= -\mathbb{x} \times \left[ \nabla \cdot \left( \mathbb{P} + \mathbb{m} \mathbb{v} \right) \right] + \mathbb{x} \times \left( \mathbb{m} f^{(\mathbb{M})} \right).
\]
(22)
For the angular momentum to be conserved,
\[
\frac{\partial \left( \mathbb{x} \times \mathbb{m} \mathbb{v} \right)}{\partial t} = -\nabla \cdot \left( \mathbb{x} \times \left( \mathbb{P} + \mathbb{m} \mathbb{v} \right) \right) + \mathbb{x} \times \left( \mathbb{m} f^{(\mathbb{M})} \right)
\]
(23)
must be satisfied, and in Appendix B, this is demonstrated to be true if and only if the pressure tensor is symmetric:
\[
\mathbb{P} = \mathbb{P}^T.
\]
(24)
Henceforth, let us assume (24) to hold.

In preparation for the next section, definition (24) of the convective derivative may be used to rewrite some of these balance laws. Employing the relation \( \nabla \cdot \mathbf{v} \) and identity (254), one may write (5) as

\[
\frac{m Dv}{Dt} = \nabla \cdot \mathbf{v}.
\]

(25)

Also, using (2), (5), and (254), one may express equations (6), (19), and (9) as

\[
\frac{m Dm}{Dt} = -\nabla \cdot \mathbf{q},
\]

(26)

\[
\frac{m Du}{Dt} = -\nabla \cdot (\mathbf{q}_{\text{heat}} + \mathbf{q}_{\text{chem}}) - P : \nabla \mathbf{v},
\]

(27)

and

\[
\frac{m Ds}{Dt} = -\nabla \cdot \mathbf{q}_S + r_S,
\]

(28)

where (24) has been assumed in equation (27).

In order to compare the foregoing balance laws with those typically postulated when deriving the Navier-Stokes-Fourier formulation, see de Groot and Mazur [16, ch. II], for example.

4 Constitutive Equations

Let us study phenomena close enough to equilibrium so that classical irreversible thermodynamics is applicable. Below, this formalism, which is detailed in de Groot and Mazur [16, ch. III and IV], is used to obtain linear non-convective constitutive equations for the fluxes.

For a single-component fluid, I propose an equilibrium fundamental relation for the entropy per mechanical mass of the form,

\[
\hat{s}(\mathbf{M}) = \tilde{s}(\mathbf{M}) \left( \hat{u}(\mathbf{M}), \hat{v}(\mathbf{M}), \hat{m}(\mathbf{M}) \right).
\]

(29)

Note the following equilibrium thermodynamic relationships,

\[
\frac{1}{T} = \frac{\partial \tilde{s}(\mathbf{M})}{\partial \hat{u}(\mathbf{M})}, \quad \frac{\hat{P}}{T} = \frac{\partial \tilde{s}(\mathbf{M})}{\partial \hat{v}(\mathbf{M})}, \quad \text{and} \quad \frac{\hat{\mu}}{T} = -\frac{\partial \tilde{s}(\mathbf{M})}{\partial \hat{m}(\mathbf{M})}.
\]

(30)

Let us assume the local equilibrium hypothesis, which implies that if \( \tilde{\alpha} \) represents any of the thermodynamic parameters mentioned above, then its corresponding local variable can be defined as

\[
\alpha = \tilde{\alpha}|_{(\mathbf{x},t)}.
\]

(31)
In particular, the fundamental equation (29) may be written locally as

\[ s(M) = \tilde{s}(M) \left( u(M), v(M), m(M) \right) \]  

(32)

which, upon taking its total differential, yields

\[ ds(M) = \frac{1}{T} du(M) + \frac{P}{T} dv(M) - \frac{\mu}{T} dm(M), \]  

(33)

provided that the differentiation is performed in a reference frame for which \( M \) is constant. Therefore, we may take the convective derivative of the above and multiply through by \( m \) to obtain

\[ m\frac{Ds(M)}{Dt} = 1_T m Du(M) + \frac{P}{T} m Dv(M) - \frac{\mu}{T} m Dm(M). \]  

(34)

Substituting equations (25)-(28) into the above and using identity (257), one arrives at the following expression for the volumetric rate of entropy production:

\[ r_S = \nabla \cdot q_S - \frac{1}{T} \nabla \cdot \left( q_{\text{heat}} + q_{\text{hem}} \right) - \frac{1}{T} \left( \mathbb{P} - \mathbb{P}_I \right) : \nabla v + \frac{\mu}{T} \nabla \cdot q_M. \]  

(35)

In the differential form of the first law of equilibrium thermodynamics, the change in energy due to heat and chemical work are represented by \( TdS \) and \( \mu dM \), respectively. With this in mind, let us take

\[ q_{\text{heat}} = T q_S \]  

(36)

and

\[ q_{\text{hem}} = \mu q_M. \]  

(37)

By employing these in equation (35) and using (20) and (254), one finds

\[ r_S = q_U \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} \left( \mathbb{P} - \mathbb{P}_I \right) : \nabla v - q_M \cdot \nabla \left( \frac{\mu}{T} \right). \]  

(38)

The second law of thermodynamics requires that

\[ r_S \geq 0 \]  

(39)

is always satisfied, and as shown in APPENDIX C, this motivates the following linear constitutive equations:

\[ q_M = -d_M \nabla \mu - \frac{k_M}{\mu} \nabla T, \]  

(40)

\[ \mathbb{P} = \mathbb{P}_I + \mathbb{P}_{\text{visc}} \]  

(41)

and

\[ q_U = -k_U \nabla T - \mu d_U \nabla \mu, \]  

(42)
in which case, \((38)\) becomes
\[
\begin{align*}
\kappa S &= \zeta T \left( \nabla \cdot \mathbf{v} \right)^2 + 2\eta T \left\| (\nabla \mathbf{v})^{\text{sym,dev}} \right\|^2 + \frac{(k_U - k_M)}{T^2} \left\| \nabla T \right\|^2 + \\
&\quad \left[ \frac{\mu (d_U - d_M)}{T^2} + \frac{k_M}{\mu T} \right] (\nabla T) \cdot (\nabla \mu) + \frac{d_M}{T} \left\| \nabla \mu \right\|^2.
\end{align*}
\]

(43)

Also in Appendix \([\text{A}]\) it is shown that Onsager reciprocity requires the coefficients to satisfy the relation,
\[
\mu (d_U - d_M) = \frac{T}{\mu} k_M.
\]

(44)

Assuming this, one may eliminate, say, \(d_U\) in equation \((43)\) to find
\[
\begin{align*}
\kappa S &= \zeta T \left( \nabla \cdot \mathbf{v} \right)^2 + 2\eta T \left\| (\nabla \mathbf{v})^{\text{sym,dev}} \right\|^2 + \frac{(k_U - k_M)}{T^2} \left\| \nabla T \right\|^2 + \\
&\quad \frac{2k_M}{\mu T} (\nabla T) \cdot (\nabla \mu) + \frac{d_M}{T} \left\| \nabla \mu \right\|^2.
\end{align*}
\]

(45)

From the above expression, it may be shown that condition \((39)\) for the second law of thermodynamics is always satisfied if
\[
\zeta, \eta, d_M, (k_U - k_M) \geq 0
\]

(46)

and
\[
d_M (k_U - k_M) \geq \frac{T}{\mu^2} k_M^2.
\]

(47)

Let us summarize these findings so far. My general formulation, which I refer to as the \(M\)-formulation, may be written as equations \((5)-(7)\) and \((19)/(20)\),
\[
\begin{align*}
\frac{\partial m}{\partial t} &= -\nabla \cdot (m \mathbf{v}) \\
\frac{\partial m}{\partial t} &= -\nabla \cdot (q_M + m \mathbf{v}) \\
\frac{\partial (\overline{\mathbf{v}})}{\partial t} &= -\nabla \cdot (\mathbf{P} + \overline{\mathbf{v}} \mathbf{v}) + \overline{\mathbf{f}}(\overline{\mathbf{m}}) \\
\frac{\partial u}{\partial t} &= -\nabla \cdot (q_U + u \mathbf{v}) - \mathbf{P} : \nabla \mathbf{v}
\end{align*}
\]

(48)

with constitutive equations \((10)-(12)\),
\[
\begin{align*}
q_M &= -d_M \nabla \mu - \frac{k_M}{\mu} \nabla T \\
p &= p I + p_{\text{isc}} \quad \text{with} \quad p_{\text{isc}} = -\zeta (\nabla \cdot \mathbf{v}) I - 2\eta (\nabla \mathbf{v})^{\text{sym,dev}} \\
q_U &= -k_U \nabla T - \mu d_U \nabla \mu,
\end{align*}
\]

(49)

where the transport coefficients, \(d_M\), \(k_M\), \(\zeta\), \(\eta\), \(k_U\), and \(d_U\) are assumed to satisfy \((44)\), \((46)\), and \((47)\). In the next section, I introduce a simple diffusion
transport model, which yields equations for all six transport coefficients that depend on only one diffusion coefficient. The $\mathbf{M}$-formulation may be shown to satisfy Galilean invariance and the conservation of angular momentum. Furthermore, the constitutive laws each satisfy the principle of objectivity required for material frame indifference. That is to say, all of the fluxes in (49) transform in the expected way under time-dependent rigid body translation and rotation.

Using the notation from §2, the Navier-Stokes-Fourier formulation may be written as

$$\frac{\partial m}{\partial t} = -\nabla \cdot (mv)$$
$$\frac{\partial (mv)}{\partial t} = -\nabla \cdot (P + mvv) + m f^{(M)}$$
$$\frac{\partial u}{\partial t} = -\nabla \cdot (q_U + uv) - P : \nabla v$$

with constitutive equations,

$$P = PI + P_{\text{visc}}$$
$$q_U = -k_F \nabla T,$$

(50)

where $k_F$ is the Fourier heat conductivity, $\zeta_{\text{NS}}$ and $\eta_{\text{NS}}$ are the Navier-Stokes bulk and shear viscosities, respectively, and $f^{(M)}$ represents the specific body force. It is clear that if one were to assume $d_M = k_M = d_U = 0$, $k_U = k_F$, $\zeta = \zeta_{\text{NS}}$, and $\eta = \eta_{\text{NS}}$ in the $\mathbf{M}$-formulation, then $m$ and $\mathbf{m}$ would be the same quantity, resulting in the Navier-Stokes-Fourier formulation above. Therefore, the Navier-Stokes-Fourier formulation may be considered as a special case of the general $\mathbf{M}$-formulation.

5 Transport Coefficients

In this section, let us make the following assumption, which I refer to as the diffusion transport assumption: the extensive quantities, mass $M$, momentum $P$, and internal energy $U$, which undergo dissipative transport, do so objectively via diffusion. That is to say their corresponding constitutive equations are each assumed to have the form,

$$q^\text{diff} = -D \nabla a,$$

(52)

or its objective part if this quantity is not material frame indifferent.

For the mass, the above assumption implies

$$q_M = -D \nabla m.$$  (53)

As detailed in Callen [9 §5.3], for example, Legendre transformations may be used to recast this in the grand canonical description, whereupon, $q_M$ becomes

$$q_M = -Dm^2 \kappa T \left[ \frac{1}{T} \left( h^{(M)} - \mu - \frac{T \sigma}{m \kappa T} \right) \nabla T + \nabla \mu \right],$$

(54)
with specific enthalpy \( h^{(M)} \), isothermal compressibility \( \kappa_T \), and thermal expansion coefficient \( \alpha_P \). Comparing (54) with (40), one obtains the following expressions for the mass transport coefficients:

\[
d_M = m^2 \kappa_T D \tag{55}
\]

and

\[
k_M = \frac{m^2 \mu \kappa_T}{T} \left( h^{(M)} - \mu - \frac{T \alpha_P}{m \kappa_T} \right) D. \tag{56}
\]

Similarly, for the internal energy, the diffusion transport assumption yields

\[
q_U = -D \nabla u \tag{57}
\]

which, in the grand canonical description, becomes

\[
q_U = -Dm \left\{ \left[ c_V + \frac{m \kappa_T}{T} \left( h^{(M)} - \frac{T \alpha_P}{m \kappa_T} \right) \left( h^{(M)} - \frac{T \alpha_P}{m \kappa_T} - \mu \right) \right] \nabla T + \frac{m \kappa_T}{T} \left( h^{(M)} - \frac{T \alpha_P}{m \kappa_T} \right) \nabla \mu \right\}, \tag{58}
\]

where \( c_V \) represents the isochoric specific heat per mass. Comparison of (58) and (42) gives the internal energy transport coefficients,

\[
k_U = m \left[ c_V + \frac{m \kappa_T}{T} \left( h^{(M)} - \frac{T \alpha_P}{m \kappa_T} \right) \right] D \tag{59}
\]

and

\[
d_U = \frac{m^2 \kappa_T}{\mu} \left( h^{(M)} - \frac{T \alpha_P}{m \kappa_T} \right) D. \tag{60}
\]

Next, let us examine the momentum under the diffusion transport assumption. Using (52) with \( \dot{z} = \frac{m v}{m} \), one finds

\[
q_{\text{diff}}^m = -D \nabla (\bar{m} \bar{v}), \tag{61}
\]

or employing identity (254) and definitions (239) and (240),

\[
q_{\text{diff}}^m = -\bar{m} D (\nabla \bar{v})^{\text{sym}} - \bar{m} D (\nabla \bar{v})^{\text{skew}} - D (\nabla \bar{m}) \bar{v}. \tag{62}
\]

With the same procedure as described in Jou et al. [23], §1.4.1, for example, one may demonstrate that the first term on the right-hand side of (62) is objective. However, the second and third terms are not. Requiring all constitutive equations to be material frame indifferent, one chooses the viscous pressure \( P_{\text{visc}} \) to be only the objective part of \( q_{\text{diff}}^m \), i.e.

\[
P_{\text{visc}} = -\bar{m} D (\nabla \bar{v})^{\text{sym}}, \tag{63}
\]

which, upon comparison with (41), yields the following expressions for the viscosity coefficients:

\[
\eta = \frac{1}{2} \bar{m} D \tag{64}
\]
and
\[ \zeta = \frac{1}{3} mD. \] (65)

To summarize, the diffusion transport assumption gives rise to equations (55), (56), (64), (65), (59), and (60) for the transport coefficients appearing in the \( M \)-formulation:

\[
\begin{align*}
    d_M &= m^2 \kappa T D \\
    k_M &= \frac{m^2 \mu \kappa T}{T} \left( \frac{h^{(M)} - \mu - \frac{T \alpha P}{m \kappa T}}{m \kappa T} \right) D \\
    \eta &= \frac{1}{2} m D \\
    \zeta &= \frac{1}{3} m D \\
    k_U &= m \left[ c_V + \frac{m \kappa T}{T} \left( \frac{h^{(M)} - \frac{T \alpha P}{m \kappa T}}{m \kappa T} \right) \left( \frac{h^{(M)} - \mu - \frac{T \alpha P}{m \kappa T}}{m \kappa T} \right) \right] D \\
    d_U &= \frac{m^2 \kappa T}{\mu} \left( \frac{h^{(M)} - \frac{T \alpha P}{m \kappa T}}{m \kappa T} \right) D.
\end{align*}
\] (66)

I refer to the above as the "diffusion transport coefficients." It is easily shown that these satisfy Onsager reciprocity condition (44) and that if \( D \geq 0 \) and there is intrinsic equilibrium thermodynamic stability, i.e. \( \kappa_T, c_V > 0 \), then conditions (46) and (47) for the second law of thermodynamics automatically hold. Substitution of (66) into constitutive equations (40)-(42) yields

\[
\begin{align*}
    q_M &= -D \left[ m^2 \kappa T \nabla \mu + \frac{m^2 \kappa T}{T} \left( \frac{h^{(M)} - \frac{T \alpha P}{m \kappa T}}{m \kappa T} \right) \nabla T \right] \\
    \underline{P} &= \underline{P}_1 - m D (\nabla \underline{u})^{sym} \\
    q_U &= -D \left\{ \left[ m c_V + \frac{m^2 \kappa T}{m^2 \kappa T} \left( \frac{h^{(M)} - \frac{T \alpha P}{m \kappa T}}{m \kappa T} \right) \left( \frac{h^{(M)} - \mu - \frac{T \alpha P}{m \kappa T}}{m \kappa T} \right) \right] \nabla T \right\}.
\end{align*}
\] (67-69)

Of course, one may use the grand canonical formalism to transform constitutive equations (67) and (69) back so that they are, again, written in terms of the variables \( m \) and \( u \). In doing so, we have our original postulations,

\[
\begin{align*}
    q_M &= -D \nabla m \\
    \underline{P} &= \underline{P}_1 - m D (\nabla \underline{u})^{sym} \\
    q_U &= -D \nabla u.
\end{align*}
\] (70-72)

Forms (70)-(72) display the fact that we have modeled the dissipative fluxes via diffusing groups of particles which transfer mass, momentum, and energy.
Notice that only one transport parameter $D$ appears\(^5\). The most prevalent transport parameter in the Navier-Stokes-Fourier formulation is the shear viscosity $\eta_{NS}$. Therefore, for convenience, let us define a dimensionless coefficient $C$ (possibly a function of thermodynamic variables) via

$$D = C \frac{\eta_{NS}}{m}.$$ \hspace{1cm} (73)

In order to match Greenspan’s \(^{15}\) sound attenuation data in the hydrodynamic regime for classical monatomic ideal gases at room temperature, for example, we take $C = 7/6$. (See §7.3.) In Appendix \(^{15}\) values of $C$ and $D$ for various types of gases and liquids are computed using ideas from §7.3, comparisons between $D$ and the self-diffusion coefficient $D_{sd}$ are made, and the temperature, pressure, and mass density dependence of $D$ is examined.

Although it upsets the underlying simplicity of the diffusion transport assumption, one may be curious to see what happens when each of the diffusion processes involves a different coefficient. This idea is explored in Appendix \(^{14}\).

6 Summary of the Equations

We have arrived at the following equations of motion for a single-component fluid near equilibrium and in the hydrodynamic regime: the $M$-formulation balance laws \(^{15}\),

$$\begin{align*}
\frac{\partial m}{\partial t} &= -\nabla \cdot \left( \vec{m} \vec{u} \right) \\
\frac{\partial m}{\partial t} &= -\nabla \cdot \left( q_M + m \vec{v} \right) \\
\frac{\partial \left( \vec{m} \vec{u} \right)}{\partial t} &= -\nabla \cdot \left( P + \vec{m} \vec{u} \vec{u} \right) + \vec{m} f(M) \\
\frac{\partial u}{\partial t} &= -\nabla \cdot \left( q_U + uu \right) - P : \nabla \vec{u}.
\end{align*}$$

Together with the diffusion transport constitutive equations \(^{70} - 72\),

$$\begin{align*}
q_M &= -D \nabla m \\
P &= P(u, m) 1 - mD \left( \nabla \vec{u} \right)^{sym} \\
q_U &= -D \nabla u.
\end{align*}$$

Substituting the constitutive equations into the balance laws, we have a system of four partial differential equations in the four unknowns, $\vec{m}$, $m$, $\vec{u}$, and $u$. In the above expression for the total pressure tensor, I have indicated that the equilibrium thermodynamic pressure, $P$, should be written in terms of the

\(^5\)Note that $D$ is not the self-diffusion coefficient, although these quantities are the same order of magnitude for gases (see Appendix \(^{15}\)).
variables, $u$ and $m$. For example, to model a classical monatomic ideal gas, one takes

$$P = \frac{2}{3} u.$$  

If the fluid has intrinsic equilibrium thermodynamic stability, then it is a straight-forward matter to use Legendre transformations in order to replace the $u$ and $m$-dependency in the above formulation with other thermodynamic variables. For example, using the Helmholtz free energy formalism, we can recast the above in terms of the four unknowns, $\overline{m}$, $m$, $\overline{p}$, and $T$; using the Gibbs free energy formalism, we can recast the above in terms of $\overline{m}$, $P$, $\overline{\mu}$, and $T$; and, as we have already seen, using the grand canonical formalism, we can recast the above in terms of $\overline{m}$, $\overline{\mu}$, $\overline{v}$, and $T$. Due to the nature of certain equations of state and/or boundary conditions, it is often more convenient to work with one of these other forms.

I hope to have motivated the proposed formulation by the simple transport mechanism underlying its constitutive equations, one that is easily generalized to model more complicated problems such as multicomponent fluid mixtures (see Appendix E). Of course, its utility nonetheless hinges on the answers to two important questions: (1) how adequately does this formulation perform in problems of fluid mechanics, and (2) are its predictions in the hydrodynamic regime quantifiably different from those found with the Navier-Stokes-Fourier formulation? Next, let us briefly highlight some of the results that have been obtained so far.

## 7 Problems in Fluid Mechanics

In all of the following sections but §7.6 problems that may be examined with low Mach number linearizations are considered. A one-dimensional linear stability analysis is carried out in §7.1 to show that my formulation is unconditionally stable provided that the diffusion parameter, $D$, is positive. In §7.2, a mass equilibration problem with no mechanical forces is studied in order to show that my formulation reduces to one of pure diffusion governed by Fick’s law. Next, low amplitude sound propagation, which is the subject of §7.3, is demonstrated to be a way of relating my diffusion parameter, $D$, to the transport parameters of the Navier-Stokes-Fourier formulation by matching attenuations in the hydrodynamic (small $Kn$) regime, thereby connecting the two theories in this sense. Obviously, therefore, sound is not a good way to distinguish between my theory and Navier-Stokes-Fourier. However, in §7.5 light scattering is shown to provide a way of testing the difference. The shifted Brillouin peaks, which correspond to the sound (phonon) part of the spectrum, are virtually indistinguishable, as one would expect, but the central Rayleigh peak predictions are significantly different. For example, in a classical monatomic ideal gas in the

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*Defining the dimensionless Mach number, $Ma$, to be the ratio of the characteristic speed in a particular problem to the fluid’s sound speed, the low Mach number regime is taken to be that in which $Ma \ll 1$. 

---
hydrodynamic regime, my theory predicts a Rayleigh peak that is about 29\% taller and narrower than the Navier-Stokes-Fourier theory (but with the same area so that the well-verified Landau-Placzek ratio remains intact). Previous experimenters, e.g. Clark [10] and Fookson et al. [17], did not study gases fully in the hydrodynamic regime, $Kn \lesssim O\left(10^{-2}\right)$, choosing instead to focus on more rarefied gases with Knudsen numbers in the range, $O\left(10^{-1}\right) \lesssim Kn \lesssim O\left(1\right)$, which extends into the slip flow and transition regimes. Therefore, in order to verify my theory, it is important to conduct a high-resolution light scattering experiment for a gas in the hydrodynamic regime.

Another striking difference in predictions arises from the non-linear steady-state shock wave problem considered in §7.6. It is well-known that for this problem, the Navier-Stokes-Fourier formulation–and all other accepted theories, for that matter–produces normalized density, velocity, and temperature shock wave profiles that are appreciably displaced from one another with the temperature profile in the leading edge of the shock, velocity behind it, and density trailing in the back. My formulation, however, predicts virtually no displacement between these three profiles in the leading edge of the shock and much less pronounced displacements in the middle and trailing end of the shock. If an experiment can be devised to measure both the structure and position of the steady shock profiles of the mass density and, say, the temperature, then this would be another decisive test between my theory and all others.

Thermophoresis, or the down-temperature-gradient motion of a macroscopic particle in a resting fluid, is discussed in §7.7. For an idealized problem, it is shown that, through the steady-state balancing of the mechanical and diffusive terms of the mass flow, my theory provides a mechanism for thermophoresis that is not present in the Navier-Stokes-Fourier formulation. In the latter type, a thermal slip boundary condition at the particle's surface is needed in order to model thermophoretic motion, whereas the former type may be used to describe this motion with a no-slip boundary condition, i.e. one in which the tangential velocity of the particle at its surface equals that of the fluid. The concept of thermal slip is based on kinetic gas theory arguments in the slip flow regime, appropriate for $Kn \gtrsim O\left(10^{-3}\right)$, yet thermophoresis is observed in gases for much smaller Knudsen numbers in the hydrodynamic regime and also in liquids. Therefore, there are obvious advantages to being able to model this problem without the thermal slip condition.

Another example in which we cancel the diffusional and convective parts of the mass flux at an impermeable boundary is considered in §7.3.1. Here, we discuss acoustic impedance at a sound barrier, as presented in Morse and Ingard [33]. In particular, it is demonstrated that my formulation allows an impermeable boundary with a non-zero normal velocity at that boundary as that which occurs in the case of non-infinite impedance.

There is one topic that remains to be introduced. As a step towards bridging the gap between microscopic and macroscopic scales in my theory, the subject of fluctuating hydrodynamics is addressed in §7.4 where it is shown that the thermodynamic interpretation of a continuum mechanical point (i.e. a point oc-
ocupied by matter and moving with velocity $v$ stemming from my formulation is fundamentally different from that of Navier-Stokes-Fourier. That is, in the Navier-Stokes-Fourier theory, a continuum mechanical point is viewed as a thermodynamic subsystem in contact with its surrounding material which acts as a heat reservoir; whereas in my theory, the surrounding material acts not only as a heat–but also a particle–reservoir. Although I did not explicitly demonstrate it in this paper, the correlation formulas in §7.4 may be used to derive the light scattering spectra which follow in §7.5.

### 7.1 Stability Analysis

Let us consider the Cartesian one-dimensional problem in which variation is assumed to be in the $x$-direction only with $v_x$ as the only non-zero component of the velocity and there are assumed to be no body forces. If we use the Helmholtz free energy formalism to recast the $M$-formulation (48) with diffusion transport constitutive equations (70)-(72) in terms of the variables, $m, m, v_x, T$, and then linearize about the constant equilibrium state, 

\begin{equation}
(m, m, v_x, T) = (m_0, m_0, 0, T_0), \tag{74}
\end{equation}

via the expansions,

\begin{align*}
\overline{m} &\approx m_0 + \varepsilon m_1 \\
m &\approx m_0 + \varepsilon m_1 \\
v_x &\approx \varepsilon v_{x,1} \\
T &\approx T_0 + \varepsilon T_1,
\end{align*}

where $\varepsilon$ is a small dimensionless parameter proportional to the Mach number, then we arrive at the following system of linear equations:

\begin{align*}
\frac{\partial m_1}{\partial t} &= -m_0 \frac{\partial v_{x,1}}{\partial x}, \tag{79} \\
\frac{\partial m_1}{\partial t} &= D_0 \frac{\partial^2 m_1}{\partial x^2} - m_0 \frac{\partial v_{x,1}}{\partial x}, \tag{80} \\
\frac{\partial v_{x,1}}{\partial t} &= -\frac{1}{m_0} \left( \frac{1}{m_0 \kappa_{T,0}} \frac{\partial m_1}{\partial x} + \frac{\alpha_{P,0}}{\kappa_{T,0}} \frac{\partial T_1}{\partial x} \right) + D_0 \frac{\partial^2 v_{x,1}}{\partial x^2}, \tag{81} \\
\frac{\partial T_1}{\partial t} &= D_0 \frac{\partial^2 T_1}{\partial x^2} - \frac{T_0 \alpha_{P,0}}{m_0 \kappa_{T,0} \varepsilon V_0} \frac{\partial v_{x,1}}{\partial x}, \tag{82}
\end{align*}

where the subscript "0" indicates that the parameter is evaluated at the constant equilibrium state (74). Note that for this linearized problem, the mechanical mass equation (79) may be uncoupled from the rest of the system, (80)-(82). Postulating a solution, 

\[
\begin{bmatrix}
m_1 \\
v_{x,1} \\
T_1
\end{bmatrix},
\]

19
to (80)-(82) that is proportional to
\[
\exp(i\kappa x + \omega t),
\]
for \(\kappa\) real and \(\omega\) complex, one obtains the dispersion relation,
\[
\omega^3 + 3D_0\kappa^2\omega^2 + \left(c_0^2 + 3D_0^2\kappa^2\right)\kappa^2\omega + D_0 \left(c_0^2 + D_0^2\kappa^2\right)\kappa^2 = 0. \tag{83}
\]
In the above, we have employed the equilibrium thermodynamic relationships,
\[
\kappa T = \frac{\gamma}{mc^2} \text{ and } \frac{T_0\alpha_P}{\kappa T c_V} = \frac{(\gamma - 1)}{\alpha_P}, \tag{84}
\]
where \(c\) is the adiabatic sound speed and \(\gamma\) represents the isobaric to isochoric ratio of specific heats. Equation (83) may be solved for \(\omega\) to obtain the three exact roots,
\[
\begin{align*}
\omega_1(\kappa) &= -D_0\kappa^2 \tag{85} \\
\omega_2(\kappa) &= -D_0\kappa^2 + ic_0\kappa \tag{86} \\
\omega_3(\kappa) &= -D_0\kappa^2 - ic_0\kappa \tag{87}
\end{align*}
\]
Clearly, if \(D_0 > 0\) (88) is satisfied, then the real parts of \(\omega_1(\kappa), \omega_2(\kappa),\) and \(\omega_3(\kappa),\) are negative for all \(\kappa,\) resulting in the unconditional stability of linearized system (80)-(82).

For comparison, carrying out a similar procedure with the Navier-Stokes-Fourier formulation (50)/(51) yields the linearization,
\[
\begin{align*}
\frac{\partial m_1}{\partial t} &= -m_0 \frac{\partial v_{x,1}}{\partial x} \tag{89} \\
\frac{\partial v_{x,1}}{\partial t} &= \left[-\frac{1}{m_0} \left(\frac{1}{m_0\kappa T,0} \frac{\partial m_1}{\partial x} + \frac{\alpha_P}{\kappa T,0} \frac{\partial T_1}{\partial x}\right) + \frac{1}{m_0} \left(\zeta_{NS,0} + 4\eta_{NS,0} \zeta_{NS,0}\right) \frac{\partial^2 v_{x,1}}{\partial x^2}\right] \tag{90} \\
\frac{\partial T_1}{\partial t} &= \frac{k_F,0}{m_0 c_V,0} \frac{\partial^2 T_1}{\partial x^2} - \frac{T_0\alpha_P,0}{m_0\kappa T,0 c_V,0} \frac{\partial v_{x,1}}{\partial x}, \tag{91}
\end{align*}
\]
with the dispersion relation,
\[
\begin{align*}
\omega^3 + \left[\frac{\zeta_{NS,0}}{m_0} + \left(\frac{4}{3} + E_u\right) \frac{n_{SS,0}}{m_0}\right] \frac{\partial n_{SS,0}}{\partial t} \frac{\partial^2 v_{x,1}}{\partial x^2} + \left(c_0^2 + E_u\right) \left(\frac{\zeta_{NS,0}}{m_0} + 3\frac{n_{SS,0}}{m_0}\right) \frac{\partial n_{SS,0}}{\partial t} \frac{\partial v_{x,1}}{\partial x} \right] \kappa^2 \omega + D_0 \left(c_0^2 + D_0^2\kappa^2\right)\kappa^2 = 0. \tag{92}
\end{align*}
\]
where \(E_u\) is the Eucken ratio defined to be
\[
E_u = \frac{k_F}{c_V\eta_{NS}}. \tag{93}
\]
\(^7\text{Note that these roots being exact enables us to construct exact Green’s functions on the infinite domain for this problem if we so desire.}\)
Let us also define the quantities,

\[ \Sigma_0 = \frac{E u_0 \eta_{NS,0}}{\gamma_0 m_0} \]  

(94)

and

\[ \Gamma_0 = \frac{1}{2} \left\{ \frac{\zeta_{NS,0}}{m_0} + \left[ \frac{4}{3} + \left( 1 - \frac{1}{\gamma_0} \right) E u_0 \right] \frac{\eta_{NS,0}}{m_0} \right\}. \]  

(95)

Using these, equation (92) yields the following three approximate roots,

\[ \omega_1 (\kappa) \approx -\Sigma_0 \kappa^2 \]  

(96)

\[ \omega_2 (\kappa) \approx -\Gamma_0 \kappa^2 + ic_0 \kappa \]  

(97)

\[ \omega_3 (\kappa) \approx -\Gamma_0 \kappa^2 - ic_0 \kappa, \]  

(98)

in the

\[ \frac{\eta_{NS,0} |\kappa|}{m_0 c_0} \ll 1 \]  

(99)

limit, which corresponds to the low Knudsen number, or hydrodynamic, regime. For an equilibrium thermodynamically stable fluid,

\[ \gamma \geq 1 \text{ and } c_V > 0 \]  

(100)

are satisfied, and therefore, if \( \eta_{NS,0}, \zeta_{NS,0}, \text{ and } k_{F,0} \) are all chosen to be non-negative, then we arrive at the well-known result that the one-dimensional linearized Navier-Stokes-Fourier formulation does not go unstable in the hydrodynamic regime.

### 7.2 Pure Diffusion

If we take the limit as the transport parameters go to zero (\( D \to 0 \) in my formulation or \( \eta_{NS}, \zeta_{NS}, k_F \to 0 \) in Navier-Stokes-Fourier), we are left with the Euler equations of pure wave motion for which, on an infinite domain, perturbations travel at the adiabatic sound speed and never decay. In the present section, we study a problem on the other end of the dichotomy, one of pure diffusion.

For this, it is instructive to bear the following example of thermodynamic equilibration in mind. Let us consider a Cartesian one-dimensional problem on the infinite domain in which the initial conditions are given by

\[ m(x,0) = \begin{cases} 
 m_0 + \delta m & \text{for } x < |a| \\
 m_0 & \text{for } x > |a| 
\end{cases} \]  

(101)

\[ v_x(x,0) = 0 \text{ for all } x \]  

(102)

\[ T(x,0) = \begin{cases} 
 T_0 + \delta T & \text{for } x < |a| \\
 T_0 & \text{for } x > |a| 
\end{cases}. \]  

(103)

This describes a perturbed subsystem initially shaped like an infinite slab, centered at \( x = 0 \) with width \( 2a \), in contact with two identical infinite reservoirs.
on either side of it. As time approaches infinity, one expects the subsystem to equilibrate with the reservoirs until the whole system has uniform mass density $m_0$ and temperature $T_0$. Let us further suppose (1) that the perturbations $\delta_m$ and $\delta_T$ are small compared to their respective equilibrium values so that it is appropriate to use the linearized equations presented in §7.1 and (2) that $\delta_m$ and $\delta_T$ are chosen to satisfy

$$\delta_m = -m_0 \alpha P_0 \delta T$$

such that the initial pressure is in equilibrium, i.e.

$$P(x, 0) = P_0$$

for all $x$.

Note that conditions (102) and (105) mean that there are initially no mechanical forces acting on the system, and so it is of interest to see, in a problem such as this, the consequences of assuming a $v_x(x, t) = 0$ solution.

To this end, let us examine the zero velocity solution,

$$v_{x,1} = 0,$$

to my linearized equations (80)-(82). Substituting (106) into the equations yields

$$\frac{\partial m_1}{\partial t} = D_0 \frac{\partial^2 m_1}{\partial x^2},$$

$$\frac{1}{m_0 \kappa T_0} \frac{\partial m_1}{\partial x} + \frac{\alpha P_0}{\kappa T_0} \frac{\partial T_1}{\partial x} = 0,$$

and

$$\frac{\partial T_1}{\partial t} = D_0 \frac{\partial^2 T_1}{\partial x^2}.$$

Equation (108) is a constraint that there are no pressure gradients and it forces the mass density and temperature perturbations to be related by

$$m_1(x, t) = -m_0 \alpha P_0 T_1(x, t)$$

as long as there exists any point at which $m$ and $T$ attain their equilibrium values, $m_0$ and $T_0$, thus causing any additive function of $t$ that may appear in (110) to be zero. (Note that at $t = 0$, (110) satisfies (104) for the problem discussed above.) As we can see, the two diffusion equations (107) and (109) are perfectly consistent with the constraint (110). Furthermore, they imply that in the absence of mechanical forces, a non-equilibrium problem, such as the one described in the previous paragraph, equilibrates by pure diffusion. Equation (107) is Fick’s law which describes diffusion driven by gradients in mass density.

By comparison, if we substitute the zero velocity solution (106) into the linearized Navier-Stokes-Fourier equations (89)-(91), then we find only the trivial solution,

$$m_1(x, t) = T_1(x, t) = 0,$$
unless we examine the special case, $\alpha_{P,0} = 0$, which yields

$$m_1(x, t) = 0$$

and

$$\frac{\partial T_1}{\partial t} = \frac{k_{F,0}}{m_0cv_{,0}} \frac{\partial^2 T_1}{\partial x^2}.$$ 

Either way, it is clear that for the initial value problem described previously, the mass density does not equilibrate via pure diffusion when the Navier-Stokes-Fourier formulation is used. In fact, a non-zero velocity solution is required.

7.3 Sound Propagation

Next, let us employ linearized system (80)-(82) to study one-dimensional Cartesian sound propagation for low amplitude sound waves of angular frequency $\omega$. For this problem, one postulates a solution proportional to

$$\exp(\kappa x + i\omega t),$$

where $\omega$ is real and $\kappa$ is complex, leading to the following dispersion relation:

$$iD_0^3\kappa^6 + D_0 (-ic_0^2 + 3D_0\omega) \kappa^4 + (-3iD_0\omega - c_0^2) \omega \kappa^2 - \omega^3 = 0. \quad (111)$$

Equation (111) may be solved to obtain six $\kappa$-roots: the propagational pair,

$$\kappa_p(\pm) (\omega) \approx \pm \frac{\omega}{c_0} \left( i + \frac{D_0\omega}{c_0^2} \right), \quad (112)$$

the thermal pair\(^8\)

$$\kappa_t(\pm) (\omega) = \pm \sqrt{\frac{\omega}{2D_0}} (1 + i), \quad (113)$$

and an extra pair,

$$\kappa_e(\pm) (\omega) \approx \pm \frac{\omega}{c_0} \left( i + \frac{c_0^2}{D_0\omega} \right). \quad (114)$$

The thermal roots (113) are exact solutions to (111), but (112) and (114) represent approximate solutions in the hydrodynamic regime, requiring

$$\frac{D_0\omega}{c_0^2} \ll 1. \quad (115)$$

Note that (112) suggests that sound attenuation experiments, such as Greenspan’s [18] and [19], may be used to measure the diffusion parameter $D$ of my formulation for various fluids under a wide variety of thermodynamic conditions.

\(^8\)As discussed in Morse and Ingard [33, §6.4], the thermal roots are used to model thermal boundary layers that may form near walls—see §7.3.1
Commonly, one finds $\alpha/f^2$ and $c$ data tabulated from such experiments at given temperatures and pressures, where

$$\alpha \equiv \text{Re} \left[ \kappa_{p(+)} \right] \quad \text{and} \quad f \equiv \frac{\omega}{2\pi}.$$  \hfill (116)

In the hydrodynamic regime, equation (112) implies the formula,

$$D_0 = \frac{c_0^3}{2\pi^2} \frac{\alpha}{f^2},$$  \hfill (117)

and in Appendix F, this formula is used together with sound propagation data to compute the diffusion parameter for a variety of selected gases and liquids.

For the Navier-Stokes-Fourier formulation, one may use the foregoing procedure to obtain the dispersion relation,

$$\left\{ \begin{array}{c}
-ic_0^2\Sigma_0 + E\nu_0 \left( \frac{\zeta_{NS,0}}{m_0} + 4 \frac{\eta_{NS,0}}{m_0} \right) \frac{\eta_{NS,0}}{m_0} \omega \\
-\left( 2\Gamma_0 + \Sigma_0 \right) \omega - c_0^2 \omega \kappa^2 - \omega^3 \end{array} \right\} \kappa^4 = 0,$$  \hfill (118)

where $\Sigma_0$ and $\Gamma_0$ are defined in equations (94) and (95). Solving equation (118), one finds four $\kappa$-roots: the propagational pair,

$$\kappa_{p(\pm)} (\omega) \approx \pm \frac{\omega}{c_0} \left( i + \frac{\Gamma_0 \omega}{c_0^2} \right),$$  \hfill (119)

and the thermal pair,

$$\kappa_{t(\pm)} (\omega) \approx \pm \sqrt{\frac{\omega}{2\Sigma_0}} \left[ \left( 1 - \frac{\Omega_0 \omega}{c_0^2} \right) i + \left( 1 + \frac{\Omega_0 \omega}{c_0^2} \right) \right],$$  \hfill (120)

where we have defined

$$\Omega_0 = \frac{1}{2} \left( 1 - \frac{1}{\gamma_0} \right) \left[ E\nu_0 \left( \frac{\eta_{NS,0}}{m_0} \right) - \gamma_0 \left( \frac{\zeta_{NS,0}}{m_0} + \frac{4}{3} \frac{\eta_{NS,0}}{m_0} \right) \right],$$  \hfill (121)

and all four roots are approximations in the hydrodynamic regime,

$$\frac{\eta_{NS,0}\omega}{m_0 c_0^2} \ll 1.$$  \hfill (122)

Note that a comparison of equations (112) and (119)/(95) gives a convenient way of relating the diffusion coefficient, $D_0$, of my formulation to the bulk and shear viscosities, $\zeta_{NS,0}$ and $\eta_{NS,0}$, and the thermal conductivity $k_{F,0}$ appearing in the Navier-Stokes-Fourier formulation, i.e. to match these predictions for sound attenuation, one chooses

$$D_0 = \Gamma_0 = \frac{1}{2} \left\{ \frac{\zeta_{NS,0}}{m_0} + \left[ 4 \left( 1 - \frac{1}{\gamma_0} \right) E\nu_0 \right] \frac{\eta_{NS,0}}{m_0} \right\}.$$  \hfill (123)

For example, in a classical monatomic ideal gas for which one typically chooses

$$\zeta_{NS,0} = 0, \quad \gamma_0 = \frac{5}{3}, \quad \text{and} \quad E\nu_0 = \frac{5}{2},$$  \hfill (124)

24
equation (123) implies
\[ D_0 = \frac{7}{6} \frac{\eta_{NS,0}}{m_0}, \]  
which in view of equation (73), written for this linearized problem as
\[ D_0 = C_0 \frac{\eta_{NS,0}}{m_0}, \]  
(126)
yields
\[ C_0 = \frac{7}{6}. \]  
(127)

Next, instead of the hydrodynamic regime approximations, (112) and (119), let us consider the exact propagational roots:
\[ \kappa_{p(+)}(\omega) = \sqrt{c_0^2 + 2iD_0\omega - c_0\sqrt{c_0^2 + 4iD_0\omega} \frac{D_2}{2D_0} - \frac{c_0^2}{c_0^2 - \gamma_{NS,0}m_0}}, \]  
(128)
corresponding to my formulation and
\[ \kappa_{p(+)}(\omega) = \sqrt{\frac{c_0^2 + 2iD_0\omega - c_0\sqrt{c_0^2 + 4iD_0\omega} \frac{D_2}{2D_0} - \frac{c_0^2}{c_0^2 - \gamma_{NS,0}m_0}}{2D_0}}, \]  
(129)
corresponding to the Navier-Stokes-Fourier formulation. \text{FIGURE 1} is a plot of the dimensionless real and imaginary parts,
\[ \alpha' = \text{Re} \left( \frac{c_0 \kappa_{p(+)}(\omega)}{\omega} \right) \]  
(130)
and
\[ \beta' = \text{Im} \left( \frac{c_0 \kappa_{p(+)}(\omega)}{\omega} \right), \]  
(131)
of the above roots versus the dimensionless parameter,
\[ r \equiv \frac{m_0 c_0^2}{\omega \gamma_{0} \eta_{NS,0}}, \]  
(132)
which is inversely proportional to the Knudsen number for a gas. The \( \alpha' \) and \( \beta' \) parameters characterize the sound attenuation and the inverse sound speed, respectively. The curves (blue for my formulation and red for Navier-Stokes-Fourier) correspond to a classical monatomic ideal gas for which (124) and (125) are chosen, as well as the equilibrium thermodynamic formula for the adiabatic sound speed,
\[ c = \sqrt{\frac{5RT}{3A}}, \]  
(133)
where $R$ is the universal gas constant and $A$ represents the atomic weight of the gas. The points are Greenspan’s [18] sound data for the noble gases, helium, neon, argon, krypton, and xenon, at room temperature. Both axes are logarithmic scale, and the upper and lower curves correspond to $\beta'$ and $\alpha'$, respectively. From Figure 1, it is clear that my theory’s sound predictions match those of the Navier-Stokes-Fourier formulation in the hydrodynamic (high $r$, or low $Kn$) regime, as intended. As I have emphasized throughout, my formulation is a continuum theory intended to be used in the $Kn \ll 1$ regime, and so I make no general claims that it works well into more rarefied higher Knudsen number regimes. However, Figure 1 provides an intriguing demonstration that for this problem, my theory does significantly better than Navier-Stokes-Fourier there. Of course, until I can provide a formal explanation, this should be viewed as strictly fortuitous.

### 7.3.1 Sound at a Boundary

Morse and Ingard [33, Chapter 6] use the Navier-Stokes-Fourier equations in order to study low amplitude sound waves hitting a wall. For easier comparison with their treatment and for general convenience, as well, let us use the Gibbs free energy formalism to recast my formulation (48)/(70)-(72) with no body forces in terms of the variables, $\overline{m}$, $P$, $v_x$, and $T$, and then linearize about the...
constant equilibrium state,
\[(m, P, v_x, T) = (m_0, P_0, 0, T_0), \tag{134}\]
via the expansions,
\[m \approx m_0 + \varepsilon m_1 \tag{135}\]
\[P \approx P_0 + \varepsilon P_1 \tag{136}\]
\[v_x \approx \varepsilon v_{x,1} \tag{137}\]
\[T \approx T_0 + \varepsilon T_1 \tag{138}\]
with \(\varepsilon\), as before, a small dimensionless parameter proportional to the Mach number. Doing so, one obtains the following system:
\[\frac{\partial m_1}{\partial t} = -m_0 \frac{\partial v_{x,1}}{\partial x} \tag{139}\]
\[\frac{\partial P_1}{\partial t} = D_0 \frac{\partial^2 P_1}{\partial x^2} - m_0 c_0^2 \frac{\partial v_{x,1}}{\partial x} \tag{140}\]
\[\frac{\partial v_{x,1}}{\partial t} = \frac{1}{m_0} \frac{\partial P_1}{\partial x} + D_0 \frac{\partial^2 v_{x,1}}{\partial x^2} \tag{141}\]
\[\frac{\partial T_1}{\partial t} = D_0 \frac{\partial^2 T_1}{\partial x^2} - \frac{T_0 \alpha P_0 \varepsilon c_0^2}{c_{P,0}} \frac{\partial v_{x,1}}{\partial x}, \tag{142}\]
where \(c_P\) is the isobaric specific heat per mass, "0" subscripts are used to indicate evaluation at the equilibrium state \((T_0, P_0)\), and the equilibrium thermodynamic relationships \((84)\) and
\[\gamma = \frac{c_P}{c_V} \tag{143}\]
have been used. Again, we see that the mechanical mass equation \((139)\) may be uncoupled from the rest of the system and postulating a solution
\[
\begin{bmatrix} P_1 \\ v_{x,1} \\ T_1 \end{bmatrix}
\]
to the remaining system \((140)-(142)\) that is proportional to
\[\exp (i\kappa x + \omega t)\]
with \(\omega\) real and \(\kappa\) complex, unsurprisingly leads to the same dispersion relation \((111)\) and the same six roots \((112)-(114)\) as before. However, when my equations are cast in the present form, one notes the following interesting fact: the temperature equation \((142)\) may be uncoupled from the pressure and velocity equations, so that the dispersion relation arising from the reduced system, \((140)\) and \((141)\), yields only the propagational roots \((112)\) and the extra roots \((114)\). The thermal roots \((113)\) arise only when the temperature equation \((142)\) is coupled back into the system. This means that within my formulation, thermal
modes of the solution may contribute only to the temperature variable and not
the pressure or velocity variables, i.e. the mechanical variables. On the other
hand, propagational and extra modes may contribute to all three.

Next, let us examine the length scales associated with each of these three
types of roots. If we compute the length scale as the distance it takes for a mode
to attenuate to $1/e$ of its amplitude, then we find the propagational, thermal,
and extra mode lengths to be

\[ d_p \equiv \frac{1}{|\text{Re} \kappa_{p(\pm)}|} = \frac{c_0^3}{4\pi^2 f^2 D_0}, \]  
\[ d_t \equiv \frac{1}{|\text{Re} \kappa_{t(\pm)}|} = \sqrt{\frac{D_0}{\pi f}}, \]

and

\[ d_e \equiv \frac{1}{|\text{Re} \kappa_{e(\pm)}|} = \frac{D_0}{c_0}, \]

respectively, where (112)-(114) and (116) have been used in the above. For
example, if we consider sound waves at frequency $f = 11$ MHz as in Greenspan
[18] and argon gas at normal temperature and pressure ($T_0 = 300$ K and $P_0 =
1.013 \times 10^5$ Pa) with $D_0 = 1.64 \times 10^{-5}$ m$^2$/s (see Appendix F) and $c_0 = 323$
$m/s$ (from the classical monatomic ideal gas formula, $c_0 = \sqrt{5RT_0/(3A)}$), then
the above length scales are computed to be

\[ d_p = 4.30 \times 10^{-4} \text{ m}, \]
\[ d_t = 6.87 \times 10^{-7} \text{ m}, \]

and

\[ d_e = 5.08 \times 10^{-8} \text{ m}. \]

In this case—and in general, for all ideal gases in the hydrodynamic regime—the
extra mode has a length scale $d_e$ roughly equal to the mean free path length of
the gas in its equilibrium state ($T_0, P_0$), regardless of sound frequency, and

\[ d_p \gg d_t > d_e. \]  

Away from boundaries, the propagational modes of sound waves dominate.
However, depending on the boundary conditions, the thermal and extra modes
may play an important role near walls, causing the formation of boundary layers
with lengths $d_t$ and $d_e$, respectively.

When the Navier-Stokes-Fourier equations are recast in the Gibbs free energy
description and linearized as above, we arrive at the following system:

\[ \frac{\partial P_1}{\partial t} = \frac{\alpha_{P,0} c_{2F,0} k_{F,0}}{c_{P,0}} \frac{\partial^2 T_1}{\partial x^2} - m_0 c_0 \frac{\partial v_{x,1}}{\partial x}, \]  
\[ \frac{\partial v_{x,1}}{\partial t} = -\frac{1}{m_0} \frac{\partial P_1}{\partial x} + \left( \frac{\zeta_{NS,0}}{m_0} + \frac{4 \eta_{NS,0}}{3 m_0} \right) \frac{\partial^2 v_{x,1}}{\partial x^2}, \]

\[ \frac{\partial T_1}{\partial t} = \frac{\gamma_{0} k_{F,0}}{m_0 c_{P,0}} \frac{\partial^2 T_1}{\partial x^2} - \frac{T_0 \alpha_{P,0} c_{0}^3}{c_{P,0}} \frac{\partial v_{x,1}}{\partial x}. \]
which again yields dispersion relation (118) and the four roots (119) and (120). Unlike in my formulation, none of the above equations uncouple from one another. Therefore, in the Navier-Stokes-Fourier formulation the two possible modes, propagational and thermal, may contribute to each of the three variables: pressure, velocity, and temperature.

Using (119) and (120), the length scales associated with the propagational and thermal modes of the Navier-Stokes-Fourier formulation are computed to be

\[
    d_p \equiv \frac{1}{|\text{Re} \kappa_p(\pm)|} = \frac{c_0^3}{4\pi^2 f^2 \Gamma_0} \quad (151)
\]

and

\[
    d_t \equiv \frac{1}{|\text{Re} \kappa_t(\pm)|} = \sqrt{\frac{\Sigma_0}{\pi f} \frac{1}{1 - 2\pi f/\Omega_0}} \quad (152)
\]

In view of (123), equation (151) yields the same propagation length as (144). Also, in the hydrodynamic regime, the thermal length given by (152) is the same order of magnitude as the thermal length (145) from my formulation.

Let us assume the \(yz\)-plane forms a sound barrier at \(x = 0\) and, as in Morse and Ingard, define the acoustic impedance of the wall as

\[
    z_w \equiv \frac{\text{acoustic pressure at wall}}{\text{normal fluid velocity at wall}} = \frac{\varepsilon P_1}{\varepsilon v_{x,1}|x=0} \quad (153)
\]

Infinite impedance corresponds to a perfectly reflected sound wave in which its outgoing velocity is equal in magnitude and opposite in direction to its incoming velocity, resulting in

\[
    \varepsilon v_{x,1}|x=0 = 0 \quad (154)
\]

For non-infinite wall impedances, however, there is a non-zero normal fluid velocity at the wall. Using my formulation, we may still consider the wall to be both stationary and impermeable by enforcing the no total mass flux condition,

\[
    j_{M,x}|x=0 = (q_{M,x} + m v_x)|x=0 = 0 \quad (155)
\]

which becomes

\[
    \left[ -D_0 \left( -m_0 \alpha_{P,0} \frac{dT_1}{dx} + \frac{\gamma_0}{c_0^2} \frac{dP_1}{dx} \right) + m_0 v_{x,1} \right]|_{x=0} = 0 \quad (156)
\]

when we assume the diffusion transport constitutive law (70), recast in the Gibbs free energy description, and linearize. On the other hand, if (154) is not satisfied in the Navier-Stokes-Fourier formulation, there arises the curious situation of a non-zero normal mass flux at \(x = 0\). Morse and Ingard [33, p.260] explain this phenomenon as follows: "The acoustic pressure acts on the surface and tends to make it move, or else tends to force more fluid into the pores of the surface." Wall movement and/or fluid lost to pores in the wall are yet never treated explicitly.
7.4 Fluctuating Hydrodynamics

The procedure for investigating stationary Gaussian-Markov processes, as described by Fox and Uhlenbeck [13], may be used to derive the formulas of fluctuating hydrodynamics for my theory. This procedure involves linearizing the three-dimensional Cartesian version of the hydrodynamic equations, interpreting the variables as fluctuating variables, and introducing zero-mean fluctuating hydrodynamic forces. This yields the following Langevin type of system:

\[
\begin{align*}
\frac{\partial (\epsilon \hat{m}_1)}{\partial t} &= -m_0 \nabla \cdot (\epsilon \hat{u}_1) + D_0 \nabla^2 (\epsilon \hat{m}_1) + \nabla \cdot \hat{R}_M \\
\frac{\partial (\epsilon \hat{u}_i)}{\partial t} &= -\nabla (\epsilon \hat{P}_i) + m_0 D_0 \nabla \cdot (\epsilon \hat{u}_i)^{sym} + \nabla \cdot \hat{R}_P, \\
\frac{\partial (\epsilon \hat{u}_j)}{\partial t} &= -m_0 h_0^{(M)} \nabla \cdot (\epsilon \hat{u}_j) + D_0 \nabla^2 (\epsilon \hat{u}_j) + \nabla \cdot \hat{R}_U. 
\end{align*}
\]

In the above, the mechanical mass density equation has been uncoupled, and inverted hats are used to distinguish the fluctuating variables from their average macroscopic continuum counterparts, e.g. \( \epsilon m_1 = \langle \epsilon \hat{m}_1 \rangle \), where \( \langle \cdot \rangle \) denotes a conditional average for a given initial condition. Also, \( \hat{R}_M, \hat{R}_P, \) and \( \hat{R}_U \) represent the fluctuating mass, momentum, and internal energy fluxes, respectively, with \( \hat{R}_P \) assumed to be symmetric and

\[
\langle \hat{R}_M \rangle = \langle \hat{R}_U \rangle = 0 \text{ and } \langle \hat{R}_P \rangle = 0. 
\]

Following the steps outlined in Fox and Uhlenbeck leads to a generalized fluctuation-dissipation theorem for stationary Gaussian-Markov processes which, when expressed for the problem at hand, yields the following correlation formulas for the Cartesian components of the fluctuating fluxes:

\[
\begin{align*}
\langle R_{M,x,} (x, t) R_{M,x,} (x', t') \rangle &= 2V (\Delta m)^2 D_0 \delta (x - x') \delta (t - t') \delta_{ij}, \\
\langle R_{U,x,} (x, t) R_{U,x,} (x', t') \rangle &= 2V (\Delta u)^2 D_0 \delta (x - x') \delta (t - t') \delta_{ij}, \\
\langle R_{M,x,} (x, t) R_{U,x,} (x', t') \rangle &= 2V (\Delta m \Delta u) D_0 \delta (x - x') \delta (t - t') \delta_{ij}, \\
\langle R_{P,x,x,} (x, t) R_{P,x,x,} (x', t') \rangle &= \begin{cases} 2k_B m_0 T_0 D_0 \delta (x - x') \delta (t - t') & \text{if } i = j = k = l \\ k_B m_0 T_0 D_0 \delta (x - x') \delta (t - t') & \text{if } i = k, j = l, i \neq j \\ k_B m_0 T_0 D_0 \delta (x - x') \delta (t - t') & \text{if } i = l, j = k, i \neq j \\ 0 & \text{otherwise} \end{cases}, \tag{162} \\
\langle R_{P,x,x,} (x, t) R_{M,x,k} (x', t') \rangle &= \langle R_{P,x,x,} (x, t) R_{U,x,k} (x', t') \rangle = 0. \tag{163} 
\end{align*}
\]

In the above formulas, the indices, \( i, j, \) and \( k \), may equal 1, 2, or 3 (the three Cartesian directions), \( \delta \) is used to represent Dirac delta distributions, \( \delta_{ij} \) is the
Kronecker delta, $k_B$ denotes the Boltzmann constant, and there appear the following equilibrium thermodynamic fluctuations:

$$
(\Delta m)^2 = \frac{k_B m_0^2 T_0 \kappa_{T,0}}{V}
$$

$$
(\Delta u)^2 = \frac{k_B m_0 T_0}{V} \left[ T_0 c_v,0 + m_0 \kappa_{T,0} \left( h_0^{(M)} - \frac{T_0 \alpha_{F,0}}{m_0 \kappa_{T,0}} \right)^2 \right] \quad (164)
$$

$$
(\Delta m \Delta u) = \frac{k_B m_0^2 T_0 \kappa_{T,0}}{V} \left( h_0^{(M)} - \frac{T_0 \alpha_{F,0}}{m_0 \kappa_{T,0}} \right),
$$

which apply to a thermodynamic system of fixed volume $V$ in contact with a heat/particle reservoir. Note the similarity in form of equations (159)-(161), involving the above fluctuations.

For comparison, the Langevin system corresponding to the Navier-Stokes-Fourier formulation is

$$
\frac{\partial (\varepsilon m)}{\partial t} = -m_0 \nabla \cdot (\varepsilon \varepsilon_i) + \nabla \cdot R_M
$$

$$
\frac{\partial (\varepsilon \varepsilon_i)}{\partial t} = \left[ -\nabla (\varepsilon P_i) + \left( \zeta_{NS,0} + \frac{\eta_{NS,0}}{m_0} \right) \nabla [\nabla \cdot (\varepsilon \varepsilon_i)] \right] + \nabla \cdot (\varepsilon \varepsilon_i)
$$

$$
\frac{\partial (\varepsilon \varepsilon_{ij})}{\partial t} = \left[ m_0 (\varepsilon) \nabla \cdot (\varepsilon \varepsilon_i) + k_F \nabla^2 (\varepsilon \varepsilon_i) + \nabla \cdot R_{ij} \right]
$$

from which one may derive Fox and Uhlenbeck’s correlations,

$$
\langle R_{M,x_i} (\mathbf{x}, t) R_{M,x_j} (\mathbf{x}', t') \rangle = 0,
$$

$$
\langle R_{U,x_i} (\mathbf{x}, t) R_{U,x_j} (\mathbf{x}', t') \rangle = 2 k_B T_0^2 k_F \delta (\mathbf{x} - \mathbf{x}') \delta (t - t') \delta_{ij},
$$

$$
\langle R_{M,x_i} (\mathbf{x}, t) R_{U,x_j} (\mathbf{x}', t') \rangle = 0,
$$

$$
\langle R_{x_i x_j} (\mathbf{x}, t) R_{x_k x_l} (\mathbf{x}', t') \rangle =
$$

$$
\begin{cases}
2 k_B T_0 \left( \frac{4 \eta_{NS,0}}{3} + \zeta_{NS,0} \right) \delta (\mathbf{x} - \mathbf{x}') \delta (t - t') \text{ if } i = j = k = l \\
2 k_B T_0 \eta_{NS,0} \delta (\mathbf{x} - \mathbf{x}') \delta (t - t') \text{ if } i = k, j = l, i \neq j \ \\
2 k_B T_0 \eta_{NS,0} \delta (\mathbf{x} - \mathbf{x}') \delta (t - t') \text{ if } i = l, j = k, i \neq j \\
2 k_B T_0 \left( \zeta_{NS,0} - \frac{2 \eta_{NS,0}}{3} \right) \delta (\mathbf{x} - \mathbf{x}') \delta (t - t') \text{ if } i = j, k = l, i \neq k \\
0 \text{ otherwise }
\end{cases}
$$

and

$$
\langle R_{x_i x_j} (\mathbf{x}, t) R_{M,x_k} (\mathbf{x}', t') \rangle = \langle R_{x_i x_j} (\mathbf{x}, t) R_{U,x_k} (\mathbf{x}', t') \rangle = 0.
$$

Therefore, in the Navier-Stokes-Fourier formulation,

$$
R_M = 0.
$$

These may be derived by using the methods in Callen [15], for example.
whereas my theory predicts a non-zero fluctuating mass flux.

This exercise illuminates certain ideas about the thermodynamic nature of a continuum mechanical point, i.e. a point occupied by matter whose motion is tracked by its local velocity, \( v \), and whose infinitesimal volume is determined by its continuum mechanical deformation. As per the local equilibrium hypothesis, near-equilibrium continuum theories are constructed under the assumption that any given continuum mechanical point may be viewed as an equilibrium thermodynamic subsystem in contact with the rest of the material which acts as a reservoir. The question as to whether or not the fluctuating mass flux \( R_M \) is zero, decides the very nature of this reservoir. All continuum theories view the surrounding material as a reservoir for heat (so that the point exchanges energy with the surrounding fluid to maintain a temperature determined by thermodynamics), but is it also a particle reservoir (so that it exchanges mass with the surrounding fluid to maintain a thermodynamically determined chemical potential)? My theory, with its non-zero \( R_M \), asserts that it is, whereas the Navier-Stokes-Fourier theory, in view of its prediction, argues that it is not, meaning that each continuum mechanical point should be conceived of as having an impermeable wall surrounding it. Although subsystems and reservoirs are abstract constructs in this setting, I believe that it makes sense to allow the mass of a continuum mechanical point to fluctuate. This view is reinforced by the natural appearance of fluctuation formulas \( 164 \) for a heat/particle reservoir in my theory’s correlations, \( 159-161 \).

Another conceptual difference between the two formulations is seen by comparing the \((i = j, k = l, i \neq k)\) case of equations \( 162 \) and \( 169 \): my theory predicts no cross-correlations between the diagonal elements of the fluctuating momentum flux, whereas Navier-Stokes-Fourier, in general, does. Furthermore, for a classical monatomic ideal gas–or any other fluid for which one assumes \( \zeta_{NS,0} < 2\eta_{NS,0}/3 \)–the Navier-Stokes-Fourier theory predicts these cross-correlations to be negative, or in other words, for the diagonal elements of the fluctuating momentum flux to be inversely correlated with one another.

### 7.5 Light Scattering

One may derive the light scattering spectra corresponding to my formulation by using the procedure in Berne and Pecora [2 §10.4]. The main steps involved are to (1) linearize the Cartesian three-dimensional equations–expressed in terms of the variables, mechanical mass \( m \), particle number density \( n_p = N_A m / A \), divergence of the velocity \( \phi = \nabla \cdot v \), and temperature \( T \)–about the constant equilibrium state, \( (m, n_p, \phi, T) = (m_0, n_{p,0}, 0, T_0) \), (172)

(2) uncouple the mechanical mass density equation, (3) take the Fourier-Laplace transform of the remaining linear system, (4) solve for the Fourier-Laplace transformed variables, and (5) use this solution to construct time-correlation functions and their spectral densities. Of particular interest is the density-density
spectrum, computed for my formulation to be exactly

$$ S_{n_p n_p} (k, \omega) = \frac{S}{\pi} \left\{ \frac{1 - \frac{1}{\gamma_0}}{2 \gamma_0} \left[ \frac{D_0 k^2}{(\omega + \omega(k))^2 + (D_0 k^2)^2} + \frac{D_0 k^2}{(\omega - \omega(k))^2 + (D_0 k^2)^2} \right] \right\}. \quad (173) $$

In the above, $k$ is the magnitude of the wave vector, $\omega$ is the angular frequency; $S$ is the structure factor defined as

$$ S = \frac{N_A m_0^2 RT_0 k T_0}{4 \pi}, \quad (174) $$

where $V$ represents the scattering volume; and $\omega (k)$ is the frequency shift of the Brillouin doublets,

$$ \omega (k) = c_0 k. \quad (175) $$

The right-hand side of (173) is the sum of three Lorentzian line shapes, the first of which is the central Rayleigh peak, and the other two, the negatively and positively $\omega (k)$-shifted Brillouin peaks. The Brillouin peaks represent light scattering due to the sound modes, or phonons, generated by pressure fluctuations, and the Rayleigh peak is caused by light being scattered from specific entropy fluctuations.

The Navier-Stokes-Fourier density-density spectrum is given by the more complicated expression,

$$ S_{n_p n_p} (k, \omega) = \frac{S}{\pi} \Re \left\{ \left\{ -\omega^2 + i \omega \left[ \frac{\zeta_{NS,0}}{m_0} + \frac{4}{3} + \Gamma_{0} \right] \frac{n_{NS,0}}{m_0} k^2 \right\} \right\}, \quad (176) $$

where $\Gamma_0$ is the Eucken ratio defined in (173). In the hydrodynamic regime for which

$$ \frac{\eta_{NS,0} k}{m_0 c_0} \ll 1, \quad (177) $$
equation (176) becomes approximately

$$ S_{n_p n_p} (k, \omega) = \frac{S}{\pi} \left\{ \frac{1 - \frac{1}{\gamma_0}}{2 \gamma_0} \left[ \frac{\zeta_{NS,0} k^2}{(\omega + \omega(k))^2 + (\Gamma_{0} k^2)^2} + \frac{\Gamma_{0} k^2}{(\omega - \omega(k))^2 + (\Gamma_{0} k^2)^2} \right] \right\}, \quad (178) $$

where $\Sigma_0$ and $\Gamma_0$ are defined in (174) and (175) and

$$ b (k) \equiv \frac{k^2}{\gamma_0 \omega (k)} \left\{ \frac{\zeta_{NS,0}}{2 m_0} + \frac{3}{2} \left( 1 - \frac{1}{\gamma_0} \right) \left[ \Gamma_{0} \frac{k^2}{m_0} + \frac{2}{3} \right] \right\}. \quad (179) $$
In approximate expression (178), the first three terms represent the Lorentzian Rayleigh and Brillouin peaks and the last two terms give a fairly small, but not negligible, non-Lorentzian contribution.

Next, as in Clark [10] and Fookson et al. [17], let us define a dimensionless angular frequency,

\[ x = \sqrt{\frac{\gamma_0}{2} \omega c_0 k} \tag{180} \]

the dimensionless uniformity parameter,

\[ y = \frac{1}{3} \sqrt{\frac{2}{\gamma_0 \eta_{NS,0} k}} \tag{181} \]

which is inversely proportional to the Knudsen number for a gas, and the dimensionless density-density spectrum,

\[ S'_{np,p} = \sqrt{\frac{2}{\gamma_0 S} S_{np,p}} \tag{182} \]

which has an area of 1 when written as a function of \( x \) and \( y \) and integrated over all \( x \). Figure 2 is a plot of the dimensionless density-density spectra, \( S'_{np,p} (x, y) \), predicted by my formulation (blue) and the Navier-Stokes-Fourier formulation (red) for a classical monatomic ideal gas with \( y = 20 \) and equations (124), (125), and (133) assumed. The arrows indicate the widths at half-height.

(Since the spectra are symmetric about the 0 frequency, only the right Brillouin peaks are shown.) Both theories predict similar Brillouin peaks, but mine has a Rayleigh peak with a maximum about 29% higher and width at half-height about 29% narrower than that of Navier-Stokes-Fourier. On the other hand, the areas under both of the Rayleigh peak predictions are the same, leading to identical Landau-Placzek ratios, i.e.

\[ \frac{\text{area of (central) Rayleigh peak}}{\text{area of both (shifted) Brillouin peaks}} = \gamma_0 - 1, \tag{183} \]

which for a classical monatomic ideal gas is 2/3. Note that in my theory, the Brillouin peaks and the Rayleigh peak all have the same width at half-height, a quantity that is inversely proportional to the lifetime of the excitation corresponding to the peak. This means that my theory predicts the same lifetime for phonons as it does for excitations caused by specific entropy fluctuations, whereas the Navier-Stokes-Fourier formulation predicts that excitations caused by specific entropy fluctuations die out sooner than the phonons (29% sooner in the case of a classical monatomic ideal gas). One other thing to note is that the Brillouin portion of my exact spectrum (173) predicts phonons corresponding exactly to the adiabatic sound speed, \( c_0 \), whereas the approximate Navier-Stokes-Fourier spectrum (178) predicts a small amount of dispersion due to

\[^{10}\text{This is to be expected since the Brillouin peaks correspond to the sound modes, and in (173) parameters were chosen such that my formulation and the Navier-Stokes-Fourier formulation gave the same sound predictions in the hydrodynamic regime.}\]
Figure 2: theoretical light scattering spectra for a classical monatomic ideal gas ($y = 20$)
to the non-Lorentzian contributions. In Figure 2, it can be observed that for a classical monatomic ideal gas, this dispersion acts to shift the Navier-Stokes-Fourier Brillouin peaks slightly toward the center frequency.

### 7.6 Shock Waves

The problem examined below strains the limits of what one should expect from the Navier-Stokes-Fourier formulation and my theory in two ways: (1) it is not near-equilibrium, which is counter to the assumption of §4 and Appendix C used to justify linear constitutive laws and (2) it is a $Kn \sim O(1)$ problem and, therefore, not in the hydrodynamic regime. Nonetheless, the Navier-Stokes-Fourier equations are commonly employed as a useful tool for investigating the internal structure of shock waves, and so it is of interest to see how predictions from my theory compare with these.

Let us consider a Cartesian one-dimensional steady-state shock wave like the one described in Zel’dovich and Raizer [45, pp.469-482] and depicted schematically in Figure 3 in a fixed reference frame. The subscript "i" is used to indicate undisturbed initial values ahead of the shock, and the subscript "f" is used for final values after the shock moves through. The initial and final fluid velocities are taken to be

$$v_{x,i} = 0 \text{ and } v_{x,f} = -v_p,$$

(184)

where $v_p$ is the constant speed of the piston generating the shock wave. For convenience, one transforms the problem into a coordinate system moving with the shock wave front as illustrated in Figure 4, where primes denote variables in the moving coordinate system and $v_s$ represents the constant speed of the shock front.

Expressing balance laws (5)-(8)/(20) with no body forces and diffusion transport constitutive equations (70)-(72) in the one-dimensional moving coordinate system, making the steady-state assumption that the time derivatives vanish, using the Helmholtz free energy formalism to cast the system in terms of the variables, $\bar{m}$, $m'$, $v_x'$, and $T'$, and employing the equilibrium thermodynamic
relationships,

\[ P = \frac{RTm}{A}, \quad u = \frac{3RTm}{2A}, \quad c_v = \frac{3R}{2A}, \quad \alpha_p = \frac{1}{T}, \quad \kappa_T = \frac{A}{RTm} \]  \hspace{1cm} (185)

for a classical monatomic ideal gas, yields the following system of ordinary differential equations:

\[ \frac{d}{dx'} (m' v' x) = 0 \]  \hspace{1cm} (186)

\[ \frac{d}{dx'} \left( -D' \frac{dm'}{dx'} + m' v'_x \right) = 0 \]  \hspace{1cm} (187)

\[ \frac{d}{dx'} \left( \frac{RT'm'}{A} - \frac{m' D' v'_x}{dx'} + \frac{v'_x}{2} \right) = 0 \]  \hspace{1cm} (188)

\[ \frac{d}{dx'} \left[ -\frac{3R}{2A} D' \frac{d(m'T')}{dx'} - \frac{m' D' v'_x}{dx'} v'_x + \left( \frac{5RT'm'}{2Am} + \frac{1}{2} v'_x^2 \right) \frac{m' v'_x}{m'} \right] = 0. \]  \hspace{1cm} (189)

For boundary conditions, let us assume that

\[ \lim_{x' \to -\infty} m' = m_i, \quad \lim_{x' \to -\infty} m' = m_i, \quad \lim_{x' \to -\infty} v'_x = v_s, \quad \text{and} \quad \lim_{x' \to -\infty} T' = T_i \]  \hspace{1cm} (190)

and

\[ \lim_{x' \to \infty} m' = m_f, \quad \lim_{x' \to \infty} m' = m_f, \quad \lim_{x' \to \infty} v'_x = v_s - v_p, \quad \text{and} \quad \lim_{x' \to \infty} T' = T_f \]  \hspace{1cm} (191)

and that all gradients, \( \frac{d\phi'}{dx'} \), vanish ahead of and behind the shock wave front, i.e.

\[ \lim_{x' \to -\infty} \frac{d\phi'}{dx'} = \lim_{x' \to \infty} \frac{d\phi'}{dx'} = 0, \]  \hspace{1cm} (192)

where \( \phi' \) may represent any of the variables, \( m', m', v'_x, \) or \( T' \). Then, by
integrating (186)-(189) from $-\infty$ to $x'$, one finds

$$m' v'_x = m_i v_s \tag{193}$$

$$D' \frac{dm'}{dx'} = \left( \frac{m'}{m} - 1 \right) m_i v_s \tag{194}$$

$$\overline{m'} D' \frac{dv'_x}{dx'} = \frac{R}{A} (T' m' - T_i m_i) + (v'_x - v_s) m_i v_s \tag{195}$$

$$\frac{3R}{2A} D'_x \frac{d(m'T')}{dx'} = \left[ \left( \frac{2RT'_x m'}{2A} - \frac{5RT_i}{2A} \right) + \frac{1}{2} (v'_x - v_s^2) \right] m_i v_s, \tag{196}$$

where (193) has been employed in writing equations (194)-(196), and by taking the limit of the above equations as $x' \to \infty$, one arrives at the relations

$$m_f = \frac{m_i v_s}{(v_s - v_p)} \tag{197}$$

$$m_f = \overline{m_f} \tag{198}$$

$$T_f = \frac{(v_s - v_p)}{v_s} \left( T_i + \frac{A}{R} v_s v_p \right) \tag{199}$$

$$v_s^2 - 4 \frac{15RT_i}{3A} = 0, \tag{200}$$

where (197) and (198) have been used to write (199), and (198) and (199) have been used to obtain (200). One solves (200) for the positive root to find the following expression for the shock speed:

$$v_s = \frac{2}{3} \left( v_p + \sqrt{v_p^2 + \frac{15RT_i}{4A}} \right). \tag{201}$$

Therefore, if the initial mass density and temperature, $m_i$ and $T_i$, and the piston speed, $v_p$, are known, then all of the relevant final values, $m_f$, $m_f$, $T_f$, and $v'_{x,f} = v_s - v_p$, may be computed via (201) and (197)-(199) for a classical monatomic ideal gas. Note that these are identical to the shock speed and final values found with the Navier-Stokes-Fourier equations.

Using the same assumptions and carrying out the foregoing procedure for the Navier-Stokes-Fourier formulation, yields the following system:

$$m' v'_x = m_i v_s \tag{202}$$

$$4 \frac{4}{3} \eta'_{NS} \frac{dv'_x}{dx'} = \frac{R}{A} (T' m' - T_i m_i) + (v'_x - v_s) m_i v_s \tag{203}$$

$$15 R \frac{4}{4A} \eta'_{NS} \frac{dT'}{dx'} = \left[ \left( \frac{5RT'_x m'}{2A} - \frac{5RT_i}{2A} \right) + \frac{1}{2} (v'_x - v_s^2) \right] m_i v_s \tag{204}$$

with the same boundary conditions as for my theory. In the above, classical monatomic ideal gas assumptions given in (124) have been used.
For this non-linear problem, my diffusion coefficient, $D'$, and the Navier-Stokes shear viscosity, $\eta_{NS}'$, may depend on state variables, e.g. it is common to express the viscosity with a temperature power law of the form (308):

$$\eta_{NS}(T) = \eta_{NS,r} \left( \frac{T}{T_r} \right)^\omega,$$

where $T_r$ is some reference temperature and $\eta_{NS,r}$ is the viscosity measured at $T_r$ (see APPENDIX F). Also, in APPENDIX F it is shown that in a classical monatomic ideal gas one might reasonably take (311):

$$D(T, m) = \frac{7}{6} \frac{\eta_{NS,r}}{m} \left( \frac{T}{T_r} \right)^\omega.$$

FIGURE 5 and FIGURE 6 contain plots of numerical solutions to dimensionless versions of (193)-(196) and (202)-(204) with their appropriate boundary conditions and power laws (308) and (311) describing the transport coefficients. The numerical method employed is iterative Newton’s method with centered differences approximating the spatial derivatives. The dimensionless variables used are

$$x'' = \frac{x'}{\lambda_i}, \quad v_x'' = \frac{v_x'}{c_i}, \quad m'' = \frac{m'}{m_i}, \quad m'' = \frac{m'}{m_i}, \quad \text{and} \quad T'' = \frac{T'}{T_i}, \quad (205)$$

where $\lambda_i$ and $c_i$ are the mean free path length and adiabatic sound speed in the initial state, and the Mach number is computed as

$$Ma = \frac{v_s}{c_i}. \quad (206)$$

Each of the figures corresponds to $Ma = 2.05$ with parameters chosen to be those of Alsmeyer [1] for his shock wave experiments in argon gas: the undisturbed initial values,

$$T_i = 300 \text{ K}$$
$$m_i = 1.07 \times 10^{-4} \text{ kg/m}^3 \text{ (corresponding to } P_i = 6.67 \text{ Pa)}$$
$$\lambda_i = 1.10 \times 10^{-3} \text{ m}$$
$$c_i = 323 \text{ m/s}$$

and the parameters appearing in (308),

$$T_r = 300 \text{ K}, \quad \eta_{NS,r} = 2.31 \times 10^{-5} \text{ kg/(m \cdot s)}, \quad \text{and} \quad \omega = 0.72.$$

The curves plotted in FIGURE 5 and FIGURE 6 are the normalized mass density, $m''' = (m' - m_i) / (m_f - m_i)$ (in blue), the normalized fluid speed, $v''' = (v_x' - v_x,i) / (v_x,f - v_x,i)$ (in green), and the normalized temperature, $T''' = (T' - T_i) / (T_f - T_i)$ (in red) versus the dimensionless position, $x''$. Since the numerical solution sets are arbitrarily positioned on the $x''$-axis, the $x'' = 0$
Figure 5: numerically computed shock wave profiles (my theory)

point is chosen to be the center of the mass density profile (the point at which the highest slope of \( m'' \) occurs). Figure 5 contains the normalized shock wave profiles predicted by my theory and Figure 6 contains those predicted by the Navier-Stokes-Fourier formulation. Comparing the curves in these two figures, one observes that the mass density, temperature, and fluid velocity profiles are much closer together in my theory than for the Navier-Stokes-Fourier formulation. This difference is perhaps most obvious in the leading edge of the shock wave (the \( x'' < 0 \) side) where my theory predicts these three profiles to be very near one another, whereas Navier-Stokes-Fourier predicts a pronounced displacement between the three with temperature leading, velocity behind it, and mass density in the back. I am unfamiliar with any direct physical arguments or experimental evidence that would explain why these profiles should be displaced in such a manner. Therefore, it would be very interesting to obtain measurements revealing the structure and position of these quantities. Experiments, such as Alsmeyer’s, which have been conducted to probe the internal structure of shock waves in a gas, measure only the mass density profile.  

\[11\]

When comparing normalized mass density profiles from my theory, Navier-Stokes-Fourier theory, and Alsmeyer’s curves fitted to experimental values, one sees that both of the continuum formulations underestimate the thickness of the shock wave. However, in view of the concerns raised at the beginning of this section, it is unreasonable to expect quantitative accuracy from a near-equilibrium continuum theory for this problem. The development of non-linear constitutive equations may aid in constructing a more realistic continuum model.
7.7 Thermophoresis

When a macroscopic particle is placed in a resting fluid with a temperature gradient, the particle tends to move in the cooler direction. This phenomenon is known as thermophoresis, and as Brenner [7] points out, it is modelled with the Navier-Stokes-Fourier formulation only by invoking a moleculely based thermal slip boundary condition. My formulation which features a non-convective mass flux, however, can provide a natural mechanism for thermophoresis even when a no-slip boundary condition is applied at the particle surface. The simplest problem that may be associated with thermophoresis is examined below using my theory. In it, gravity and possible boundary layers are neglected, and only small temperature gradients are considered. Also, the thermophoretic particle is assumed to be insulated and to have a radius, $R$, much larger than the fluid's mean free path length, $\lambda$, so that the Knudsen number, defined for this problem as $Kn = \lambda/R$, is small.

Let us consider a Cartesian one-dimensional problem in which a fluid at average pressure, $P_0$, lies between two parallel plates, a colder plate at $x = 0$ maintained at temperature, $T_{\text{cold}}$, and a hotter plate at $x = L$ kept at temperature, $T_{\text{hot}}$, as shown in Figure 6. Also, assume the temperature of the fluid at the plates equals that of the plates, yielding the boundary conditions,

$$T|_{x=0} = T_{\text{cold}} \text{ and } T|_{x=L} = T_{\text{hot}},$$

(207)
and let us define the dimensionless parameter,
\[
\varepsilon = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_0},
\]
where \(T_0\) is the average temperature,
\[
T_0 = \frac{T_{\text{hot}} + T_{\text{cold}}}{2}.
\]
The plates are assumed to be impermeable, i.e. allowing no mass to flow through them, which requires
\[
j_{M,x} = q_{M,x} + m v_x = 0 \text{ at } x = 0 \text{ and } x = L.
\]
It is most convenient to study this problem with the linearized Gibbs free energy description of my formulation, i.e. equations (139)-(142), used in §7.3.1. Here, the linearization is about the constant average state,
\[
(m, P, v_x, T) = (m_0, P_0, 0, T_0),
\]
and \(\varepsilon\) is taken to be the parameter defined in (208) and assumed to be small. Note that in equations (139)-(142), "0" subscripts are used to indicate evaluation at the average state, \((T_0, P_0)\). Assuming steady-state conditions, the time derivatives appearing on the left-hand side of (139)-(142) vanish, in which case these equations, together with the temperature boundary conditions (207) and definitions (208) and (209), yield the solutions,
\[
v_{x,1} = \text{constant}
\]
\[
P_1 = 0
\]
\[
T_1 = \frac{T_0}{L} \left( x - \frac{L}{2} \right).
\]
One finds an expression for the constant velocity, by enforcing the linearized version of the no mass flow condition (210):

$$- D_0 \left( - m_0 \alpha P_0 \frac{dT_1}{dx} + \gamma_0 \frac{dP_1}{dx} \right) + m_0 v_{x,1} = 0, \quad (215)$$

where the diffusion transport constitutive law (70) has been assumed and recast in the Gibbs free energy description. Substituting (213) and (214) into the above and using (137) and (208) yields

$$v_x = - D_0 \alpha P_0 \left( \frac{T_{\text{hot}} - T_{\text{cold}}}{L} \right). \quad (216)$$

Therefore, my theory predicts a constant velocity in the $-x$ (colder) direction that is proportional to the fluid’s diffusion coefficient and thermal expansion coefficient and the size of the temperature gradient imposed between the plates. If an insulated macroscopic particle were present in such a velocity field with a no-slip condition applied at its surface, then the particle would simply be carried along at the fluid’s velocity, i.e. the particle’s thermophoretic velocity, $v_{x,\text{th}}$, would equal the fluid’s continuum velocity, $v_x$, computed above.

In contrast, when the non-convective mass flux is assumed to be zero, as in the case of the Navier-Stokes-Fourier formulation, the no mass flow condition (210) yields

$$v_x = 0. \quad (217)$$

Consequently, thermophoretic motion does not arise in the same sense that it does for my theory. To account for thermophoresis with the Navier-Stokes-Fourier equations, one then finds it necessary to employ a thermal slip boundary condition at the particle’s surface at which there is assumed to be a non-zero tangential velocity proportional to the temperature gradient and in the down-gradient direction. Under this assumption, various researchers have been led, theoretically and experimentally, to the following expression for the thermophoretic velocity in the case of an insulated particle in a gas:

$$v_{x,\text{th}} = - C_{\text{th}} \frac{\eta_{\text{NS}}}{m_0 T_0} \nabla T, \quad (218)$$

where $C_{\text{th}}$ is the thermal slip coefficient, dimensionless and theoretically believed to lie in the interval, $0.75 \leq C_{\text{th}} \leq 1.5$, with $C_{\text{th}} \approx 1.17$ being a widely accepted theoretical estimate for gases. For the problem considered here, (218) becomes

$$v_{x,\text{th}} = - C_{\text{th}} \frac{\eta_{\text{NS},0}}{m_0 T_0} \left( \frac{T_{\text{hot}} - T_{\text{cold}}}{L} \right). \quad (219)$$

---

12This is, of course, a gross oversimplification of the real problem of thermophoresis in that we have neglected any and all properties of the particle. In experiment, there is no such thing as a perfectly insulated particle. Indeed, the particle’s ability to conduct heat plays an important role in determining the thermophoretic velocity.

13See Brenner and Bielenberg [5], Brenner [7], and Derjaguin et al. [13].
Employing (126) and assuming an ideal gas for which
\[ \alpha P,0 = 1/T_0, \] (220)
the thermophoretic velocity predicted by my theory in equation (216) may be expressed as
\[ v_{x,th} = -C_0 \eta_{NS,0} \frac{T_{hot} - T_{cold}}{m_0 T_0} \alpha P,0 \left( \frac{T_{hot} - T_{cold}}{L} \right). \] (221)

Therefore, by identifying \( C_0 \) with \( C_{th} \), one finds this to be the same as the thermal slip formula (219). Also, recall that in section 7.3, the value \( C_0 = 7/6 \approx 1.17 \) was obtained for a classical monatomic ideal gas.

As discussed in Brenner [7], there is no real theory for thermal slip in a liquid. Therefore, researchers, e.g. McNab and Meisen [31], typically apply the gas formulas to liquids, even though they admit that there is no theoretical justification for doing so. For the idealized problem considered here, McNab and Meisen’s data corresponds to a thermal slip coefficient for water and n-hexane near room temperature of \( C_{th} \approx 0.13 \), an order of magnitude smaller than that of a gas. Again using (126), but no longer assuming the ideal gas formula (220), my theory’s thermophoretic velocity (216) becomes
\[ v_{x,th} = -C_0 \frac{\eta_{NS,0} \alpha P,0}{m_0 T_0} \left( \frac{T_{hot} - T_{cold}}{L} \right), \] (222)
which when compared with the thermal slip formula (219), yields the relationship,
\[ C_{th} = C_0 T_0 \alpha P,0. \] (223)

For water at \( T_0 = 293 \) K, we take \( C_0 = 2.1 \) (see Appendix F) and \( \alpha P,0 = 2.05 \times 10^{-4} \) K\(^{-1} \) (from the CRC Handbook of Chemistry and Physics [12]), giving a slip coefficient value of \( C_{th} = 0.13 \), which is the same as the experimental value mentioned above.

It is interesting to note that there is, in general, no positive definite restriction on the thermal expansion coefficient \( \alpha P,0 \). There exist equilibrium thermodynamic states in water and liquid helium, for example, in which \( \alpha P,0 \) may vanish or become negative. In view of equation (223), this means that such states could give rise to the occurrence of no thermophoresis or negative thermophoresis.

### A Tensors

In this appendix, indicial notation is used in which sums are taken over repeated indices. The indices may assume the values 1, 2, or 3, representing the three spatial directions.

---

\(^{14}\)Values of \( C_0 \) pertaining to a few other types of gases are provided in Appendix F.
Algebraic Operators

- dots and contraction operators:

\[
\begin{align*}
  u \cdot w &= u_i w_i \quad (224) \\
  (T \cdot w)_i &= T_{ij} w_j \quad (225) \\
  (w \cdot T)_i &= w_j T_{ji} \quad (226)
\end{align*}
\]

\[
\begin{align*}
  T \cdot U &= T_{ij} U_{ij} \quad (227) \\
  U : T &= T_{ij} U_{ji} \quad (228)
\end{align*}
\]

\[
\begin{align*}
  C_{1,2} (T) &= T_{ii} = \text{tr} (T) \quad (229) \\
  C_{1,3} (D) &= D_{iji} \quad (230)
\end{align*}
\]

If \( A \) and \( B \) are tensors of order \( M \) and \( N \), respectively, with \( M \geq N \), then

\[
\begin{align*}
  [A \cdot B]_{i_1 \ldots i_M} &= A_{i_1 \ldots i_{M-N}} B_{i_{M-N+1} \ldots i_M} \quad (231)
\end{align*}
\]

- norms:

\[
\|w\| = \sqrt{w \cdot w} \quad \text{and} \quad \|T\| = \sqrt{T \cdot T} \quad (232)
\]

- tensor product:

\[
(u \cdot w)_{ij} = u_i w_j \quad (233)
\]

- cross products:

\[
\begin{align*}
  (u \times w)_i &= u_j w_k \varepsilon_{ijk} \quad (234) \\
  (w \times T)_{ij} &= w_k T_{il} \varepsilon_{jkl} \quad (235) \\
  (T \times U)_{ijk} &= T_{il} U_{jm} \varepsilon_{klm} \quad (236)
\end{align*}
\]

where \( \varepsilon_{ijk} \) is the alternating symbol,

\[
\varepsilon_{ijk} = \begin{cases} 
1 & \text{if } (i, j, k) = (1, 2, 3), (2, 3, 1), \text{ or } (3, 1, 2) \\
-1 & \text{if } (i, j, k) = (1, 3, 2), (2, 1, 3), \text{ or } (3, 2, 1) \\
0 & \text{if any of the indices are repeated}
\end{cases} \quad (237)
\]

The transpose, symmetric part, skew-symmetric part, spherical part, and deviatoric part of a tensor are defined by

\[
\begin{align*}
  (T^T)_{ij} &= T_{ji} \quad (238) \\
  T_{\text{sym}} &= \frac{1}{2} (T + T^T) \quad (239) \\
  T_{\text{skew}} &= \frac{1}{2} (T - T^T) \quad (240) \\
  T_{\text{sph}} &= \frac{1}{3} \text{tr} (T) I \quad (241) \\
  T_{\text{dev}} &= T - T_{\text{sph}} \quad (242)
\end{align*}
\]
and the second-order identity tensor is defined as
\[
(1)_{ij} = \delta_{ij}.
\] (243)
where \( \delta_{ij} \) is the Kronecker delta,
\[
\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}.
\] (244)

**Differential Operators**

- gradients (Cartesian coordinate definitions):
  \[
  (\nabla \alpha)_i = \frac{\partial \alpha}{\partial x_i}
  \] (245)
  \[
  (\nabla w)_{ij} = \frac{\partial w_j}{\partial x_i}
  \] (246)

- divergences (Cartesian coordinate definitions):
  \[
  \nabla \cdot w = \frac{\partial w_i}{\partial x_i}
  \] (247)
  \[
  (\nabla \cdot T)_i = \frac{\partial T_{ji}}{\partial x_j}
  \] (248)

- convective derivative:
  \[
  \frac{Df}{Dt} = \frac{\partial f}{\partial t} + v \cdot \nabla f
  \] (249)

- generalized partial derivative: If \( A \) and \( B \) are tensors of order \( M \) and \( N \), respectively, then
  \[
  \left( \frac{\partial A}{\partial B} \right)_{i_1 \ldots i_M j_1 \ldots j_N} = \frac{\partial A_{i_1 \ldots i_M}}{\partial B_{j_1 \ldots j_N}}.
  \] (250)

**Identities**

\[
\nabla \cdot (T \cdot w) = w \cdot (\nabla \cdot T) + T \cdot \nabla w = w \cdot (\nabla \cdot T) + T^T : \nabla w
\] (251)
\[
(u \cdot w) \cdot \nabla w = u \cdot \nabla w \cdot v
\] (252)
\[
\nabla \cdot (\alpha w) = \alpha \nabla \cdot w + (\nabla \alpha) \cdot w
\] (253)
\[
\nabla (u \cdot w) = (\nabla u) \cdot w + (\nabla w) \cdot u
\] (254)
\[
\nabla \cdot (w \times T) = w \times (\nabla \cdot T) + C_{1,3} \left[ (\nabla w) \times T \right]
\] (255)
\[
\nabla \cdot w = \frac{1}{V} \nabla w
\] (256)
\[
\nabla (\alpha \beta) = \alpha \nabla \beta + \beta \nabla \alpha
\] (257)
\[
T^{\text{dev}} : U = T^{\text{dev}} : U^{\text{sym}, \text{dev}} \text{ if } T = T^T
\] (258)
B  Computation for $\S 3$

**Kinetic Energy**

Taking the partial time derivative of $k$ as defined by (13) and using the product rule, we find

$$\frac{\partial k}{\partial t} = v \cdot \frac{\partial (mv)}{\partial t} - \frac{1}{2} \|v\|^2 \frac{\partial m}{\partial t}$$

or, substituting (7) and (5) into the above,

$$\frac{\partial k}{\partial t} = -v \cdot \left[ \nabla \cdot \left( P + mv v \right) \right] + m f^{(T)} \cdot v + \frac{1}{2} \|v\|^2 \nabla \cdot \left( mv \right)$$

One can then use tensor identities (251) and (254) to obtain

$$\frac{\partial k}{\partial t} = -\nabla \cdot \left[ P \cdot v + (v \cdot v) \cdot v \right] + P^T : \nabla v + m (v \cdot v) \cdot \nabla v +$$

$$m v \cdot f^{(T)} + \nabla \cdot \left( \frac{1}{2} m \|v\|^2 \right) - \frac{1}{2} m v \cdot \nabla \cdot \left( v \cdot v \right).$$

Finally, if we employ tensor identities (252) and (255), then we arrive at equation (14).

**Angular Momentum**

With the aid of tensor identity (256), the first term on the right-hand side of (22) may be written as

$$-v \times \left[ \nabla \cdot \left( P + mv v \right) \right] = -\nabla \cdot \left[ v \times \left( P + mv v \right) \right] + C_{1,3} \left[ 1 \times P \right] +$$

$$C_{1,3} \left[ 1 \times (mv v) \right], \quad (260)$$

using the fact that

$$\nabla v = \frac{1}{v}$$

and the linearity of the contraction operator, $C_{1,3}$. Next, by writing out its components, it is observed that

$$C_{1,3} \left[ 1 \times T \right] = 0$$

is satisfied if and only if $T$ is symmetric. Therefore, the symmetry of $mvv$ causes the third term on the right-hand side of (260) to vanish. Furthermore, the second term also vanishes, implying conservation of momentum (23), if and only if $P$ is symmetric.

**C  Linear Constitutive Laws**

Here, classical irreversible thermodynamics, as described in de Groot and Mazur [16, CH.III and IV] and Jou et al. [23, §1.3], is used to derive linear constitutive laws (40)-(42).
Recall equation (38) for the volumetric entropy production rate and note that
the second term on the right-hand side suggests the following decomposition for
the pressure tensor of a fluid:

\[ P = P_1 + P_{\text{visc}}, \]  \hspace{1cm} (261)

where \( P_{\text{visc}} \) represents the viscous part of the pressure, assumed symmetric, i.e.

\[ P_{\text{visc}} = P_{\text{visc}}^T, \]  \hspace{1cm} (262)

so that condition (24) is satisfied, and \( P \), as before, denotes the equilibrium
thermodynamic pressure. Consequently, equation (38) becomes

\[ r_S = q_U \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} P_{\text{visc}} : \nabla \mu - q_M \cdot \nabla \left( \frac{\mu}{T} \right). \] \hspace{1cm} (263)

One can further decompose the viscous pressure into its spherical and deviatoric
parts via

\[ P_{\text{visc}} = P_{\text{visc}}^{\text{sph}} + P_{\text{visc}}^{\text{dev}}, \] \hspace{1cm} (264)

with

\[ P_{\text{visc}}^{\text{sph}} = p_{\text{visc}} \mathbb{I} \] \hspace{1cm} (265)

where \( p_{\text{visc}} \equiv \frac{1}{3} \text{tr} \left( P_{\text{visc}} \right). \)

Substituting (264) and (265) into (263) and using identity (257) yields

\[ r_S = q_U \cdot \nabla \left( \frac{1}{T} \right) + p_{\text{visc}} \left[ - \frac{1}{T} \nabla \cdot \nabla \mu \right] + P_{\text{visc}}^{\text{dev}} : \left[ - \frac{1}{T} (\nabla \nu)^{\text{sym,dev}} \right] + q_M \cdot \left[ - \nabla \left( \frac{\mu}{T} \right) \right], \] \hspace{1cm} (266)

where property (262) has been employed in conjunction with tensor identity (259).

The terms have been grouped as in expression (266) so that \( r_S \) has the form,

\[ r_S = \sum_j F^{(j)} \cdot A^{(j)}, \] \hspace{1cm} (267)

where \( F^{(j)} \) and \( A^{(j)} \) represent fluxes and the affinities, respectively. One requires
the affinities to be objective tensor quantities and for there to exist equilibrium states for which the affinities and fluxes simultaneously vanish. Comparing (267) and (266) suggests the following identifications:

| \( j \) | \( F^{(j)} \) (flux) | \( A^{(j)} \) (affinity) |
|-----|-----------------|-----------------|
| 1   | \( F^{(1)} = q_U \) | \( A^{(1)} = \nabla \left( \frac{1}{T} \right) \) |
| 2   | \( F^{(2)} = p_{\text{visc}} \) | \( A^{(2)} = - \frac{1}{T} \nabla \cdot \nabla \mu \) |
| 3   | \( F^{(3)} = P_{\text{visc}}^{\text{dev}} \) | \( A^{(3)} = - \frac{1}{T} (\nabla \nu)^{\text{sym,dev}} \) |
| 4   | \( F^{(4)} = q_M \) | \( A^{(4)} = - \nabla \left( \frac{\mu}{T} \right) \) |

(268)
Note that $A^{(1)}$, $A^{(2)}$, $A^{(3)}$, and $A^{(4)}$ are each indeed objective tensor quantities. Next, let us assume that the fluxes are written as

$$F^{(j)} = \tilde{F}^{(j)} \left( A^{(1)}, A^{(2)}, \ldots ; T \right), \quad (269)$$

where $T$ represents a list of state parameters, each evaluated at $(x, t)$, e.g. \{\(T, m\)\} or \{\(T, P\)\}. The assumption that the affinities and fluxes vanish in a state of equilibrium implies

$$\tilde{F}^{(j)} \left( A^{(1)}, A^{(2)}, \ldots ; T \right) \bigg|_{A^{(1)}=0, A^{(2)}=0, \ldots} = 0 \quad (270)$$

so that we obtain the following expansions for the fluxes about the equilibrium state:

$$F^{(j)} = \sum_k \frac{\partial \tilde{F}^{(j)}}{\partial A^{(k)}} \left( A^{(1)}, A^{(2)}, \ldots ; T \right) \bigg|_{A^{(1)}=0, A^{(2)}=0, \ldots} \cdot A^{(k)} + (2^{nd}-order \text{ terms and higher}) \quad (271)$$

Assuming the magnitudes of the affinities are small enough to neglect the higher-order terms and defining the phenomenological coefficients as

$$L^{(jk)} (T) = \frac{\partial \tilde{F}^{(j)}}{\partial A^{(k)}} (0, 0, \ldots ; T), \quad (272)$$

equation (271) becomes the linear constitutive law,

$$F^{(j)} = \sum_k L^{(jk)} (T) \cdot A^{(k)}. \quad (273)$$

With the use of table (268), the linear constitutive laws for our single-component viscous fluid are given by

$$q_U = L^{(11)} \cdot \nabla \left( \frac{1}{T} \right) + L^{(12)} \left( -\frac{1}{T} \nabla \cdot \mathbf{u} \right) + L^{(13)} \cdot \left[ -\frac{1}{T} (\nabla \mathbf{u})^{sym, dev} \right] +$$

$$L^{(14)} \cdot \left[ -\nabla \left( \frac{\mu}{T} \right) \right], \quad (274)$$

$$p_{visc} = L^{(21)} \cdot \nabla \left( \frac{1}{T} \right) + L^{(22)} \left( -\frac{1}{T} \nabla \cdot \mathbf{u} \right) + L^{(23)} \cdot \left[ -\frac{1}{T} (\nabla \mathbf{u})^{sym, dev} \right] +$$

$$L^{(24)} \cdot \left[ -\nabla \left( \frac{\mu}{T} \right) \right], \quad (275)$$

$$p_{devvisc} = L^{(31)} \cdot \nabla \left( \frac{1}{T} \right) + L^{(32)} \left( -\frac{1}{T} \nabla \cdot \mathbf{u} \right) + L^{(33)} \cdot \left[ -\frac{1}{T} (\nabla \mathbf{u})^{sym, dev} \right] +$$

$$L^{(34)} \cdot \left[ -\nabla \left( \frac{\mu}{T} \right) \right], \quad (276)$$

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and

\[ q_M = L^{(41)} \cdot \nabla \left( \frac{1}{T} \right) + L^{(42)} \left( -\frac{1}{T} \nabla \cdot \mathbf{v} \right) + L^{(43)} \cdot \left[ -\frac{1}{T} (\nabla \mathbf{v})^{\text{sym,dev}} \right] + L^{(44)} \cdot \left[ -\nabla \left( \frac{\mu}{T} \right) \right] . \]  

(277)

As discussed in de Groot and Mazur [10, Ch.VI], in the absence of external magnetic fields and Coriolis forces, Onsager reciprocity requires that the phenomenological coefficients appearing in the above satisfy

\[ L^{(jk)} = \left\{ \begin{array}{ll} L^{(kj)} & \text{for } (j, k) = (1, 1), (1, 4), (2, 2), (2, 3), (3, 3), (4, 1), (4, 4) \\ -L^{(kj)} & \text{for } (j, k) = (1, 2), (1, 3), (2, 1), (2, 4), (3, 1), (3, 4), (4, 2), (4, 3) \end{array} \right. \]  

(278)

Furthermore, as discussed in Segel [38, §2.1], isotropic materials like fluids possess isotropic tensors for each of their phenomenological coefficients, \( L^{(-\cdot)} \), and this reduces equations (274)-(277) to

\[ q_U = L^{(11)} \cdot \nabla \left( \frac{1}{T} \right) + L^{(14)} \cdot \left[ -\nabla \left( \frac{\mu}{T} \right) \right] , \]  

(279)

\[ p_{\text{visc}} = L^{(22)} \left( -\frac{1}{T} \nabla \cdot \mathbf{v} \right) , \]  

(280)

\[ P^{\text{dev}}_{\text{visc}} = L^{(33)} \cdot \left[ -\frac{1}{T} (\nabla \mathbf{v})^{\text{sym,dev}} \right] , \]  

(281)

and

\[ q_M = L^{(41)} \cdot \nabla \left( \frac{1}{T} \right) + L^{(44)} \cdot \left[ -\nabla \left( \frac{\mu}{T} \right) \right] \]  

(282)

with

\[ L^{(11)}_{ij} = \mathcal{C}^{(11)}_{ij} \delta_{ij} , \]  

(283)

\[ L^{(14)}_{ij} = \mathcal{C}^{(14)}_{ij} \delta_{ij} , \]  

(284)

\[ L^{(41)}_{ij} = \mathcal{C}^{(41)} \delta_{ij} \]  

(285)

assuming Onsager reciprocity,

\[ L^{(44)}_{ij} = \mathcal{C}^{(44)}_{ij} \delta_{ij} , \]  

(286)

and

\[ L^{(33)}_{ijkl} = 2\mathcal{C}^{(33)} \left[ -\frac{1}{3} \delta_{ij} \delta_{kl} + \frac{1}{2} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \right] \]  

(288)

for scalars, \( \mathcal{C}^{(11)}, \mathcal{C}^{(14)}, \mathcal{C}^{(41)}, \mathcal{C}^{(44)}, \mathcal{C}^{(33)} \), and where \( \delta_{ij} \) represents the Kronecker delta.
Substituting (283) and (284) into equation (279), one finds

$$ q_U = \mathcal{L}(11) \nabla \left( \frac{1}{T} \right) - \mathcal{L}(14) \nabla \left( \frac{\mu}{T} \right) $$

$$ = \left( - \frac{\mathcal{L}(11)}{T^2} + \frac{\mu \mathcal{L}(14)}{T^2} \right) \nabla T - \frac{\mathcal{L}(14)}{T} \nabla \mu, \quad (289) $$

whereby defining

$$ k_U \equiv \frac{1}{T^2} \left( \mathcal{L}(11) - \mu \mathcal{L}(14) \right) \quad (290) $$

and

$$ d_U = \frac{\mathcal{L}(14)}{\mu T} \quad (291) $$

one obtains equation (42).

Similarly, if one employs (286) and (287), then equation (282) becomes

$$ q_M = \mathcal{L}(14) \nabla \left( \frac{1}{T} \right) - \mathcal{L}(44) \nabla \left( \frac{\mu}{T} \right) $$

$$ = \left( - \frac{\mathcal{L}(14)}{T^2} + \frac{\mu \mathcal{L}(44)}{T^2} \right) \nabla T - \frac{\mathcal{L}(44)}{T} \nabla \mu \quad (292) $$

and, therefore, defining

$$ d_M = \frac{\mathcal{L}(44)}{T} \quad (293) $$

and

$$ k_M \equiv \frac{\mu}{T^2} \left( \mathcal{L}(14) - \mu \mathcal{L}(44) \right) \quad (294) $$

yields equation (40). Note that equations (291), (293), and (294) imply the relation,

$$ k_M = \frac{\mu^2}{T^2} (d_U - d_M) \quad (295) $$

which is a consequence of the Onsager reciprocity.

Next, let us substitute (288) into (281) to find

$$ P_{\text{dev,visc}}^{\text{visc}}_{ij} = -\frac{2 \mathcal{L}(33)}{T} \left[ \frac{1}{3} \delta_{ij} \delta_{kl} + \frac{1}{2} \left( \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \right) \right] \nabla v_{\text{sym,dev}}^{\text{sym,dev}} $$

$$ = \frac{2 \mathcal{L}(33)}{3T} \text{tr} \left[ \nabla v_{ij}^{\text{sym,dev}} \delta_{ij} - \mathcal{L}(33) \frac{T}{T} \nabla v_{ij}^{\text{sym,dev}} + \nabla v_{ij}^{\text{sym,dev}} \right], $$

which implies

$$ P_{\text{dev,visc}} = -\frac{2 \mathcal{L}(33)}{T} (\nabla v_{ij}^{\text{sym,dev}} \right), $$

since the trace of any deviatoric tensor is zero. If one defines

$$ \eta \equiv \frac{\mathcal{L}(33)}{T} \quad (297) $$
and

\[ \zeta \equiv \frac{L^{(22)}}{T}, \quad (298) \]

then \((296)\) and \((280)\) become

\[ P_{\text{dev}}^{\text{visc}} = -2\eta (\nabla v)^{\text{sym,dev}} \quad (299) \]

and

\[ p_{\text{visc}} = -\zeta \nabla \cdot \mathbf{u} \quad (300) \]

Finally, using the two equations above, together with \((265)\), \((264)\), and \((261)\), one arrives at equation \((41)\) for the total pressure.

\[ \text{D Thermodynamic and Momentum Diffusion} \]

It is easily shown that if the mass and internal energy fluxes are chosen as

\[ q_M = -D_M \nabla m \quad \text{and} \quad q_U = -D_U \nabla u, \quad (301) \]

then Onsager reciprocity condition \((44)\) cannot be satisfied unless

\[ D_M = D_U. \quad (302) \]

Furthermore, constitutive equations \((67)\) and \((69)\) may be used to prove that similar flux laws hold for other thermodynamic extensive quantities, as well, e.g. the entropy, for which

\[ q_S = -D \nabla s. \quad (303) \]

Consequently, I call \((55)\), \((56)\), \((59)\), and \((60)\), "thermodynamic diffusion transport coefficients," and \((67)\) and \((69)\), or the more compactly expressed, \((70)\) and \((72)\), "thermodynamic diffusion flux laws." On the other hand, there is nothing obvious to prevent the choice of a different diffusion coefficient, \(D_P\), to be associated with the viscous pressure. In this case, the "momentum diffusion transport coefficients," \((64)\) and \((65)\), may be written as

\[ \eta = \frac{1}{2m}D_P \quad (304) \]

and

\[ \zeta = \frac{1}{3m}D_P \quad (305) \]

and the "momentum diffusion flux law" \((71)\) as

\[ P = P_{\text{I}} - \overline{mD_P} (\nabla u)^{\text{sym}}. \quad (306) \]

Of course, the diffusion transport fluxes are found by choosing thermodynamic and momentum diffusion fluxes with \(D_P = D\).
Multicomponent Fluid Mixtures

To model a multicomponent mixture of fluids, one may use the same ideas as those used to obtain (48)/(70)-(72). Let $M_i$ represent the mass of component $i$ in an $N$-component mixture. For an $N$-component fluid near equilibrium and in the continuum regime, I propose the $M$-formulation balance laws,

\[
\begin{align*}
\frac{\partial m}{\partial t} &= -\nabla \cdot (\overline{m} \overline{v}) \\
\frac{\partial m_i}{\partial t} &= -\nabla \cdot (q_{M_i} + m_i \overline{v}) \quad \text{for } i = 1, \ldots, N \\
\frac{\partial (\overline{m} \overline{u})}{\partial t} &= -\nabla \cdot (P - \overline{m} \overline{v} \cdot \overline{u}) + \overline{m} f(M) \\
\frac{\partial u}{\partial t} &= -\nabla \cdot (q_{M_i} + u \overline{v}) - P : \nabla \overline{v}
\end{align*}
\]

with diffusion transport constitutive equations,

\[
\begin{align*}
q_{M_i} &= -D \nabla m_i \quad \text{for } i = 1, \ldots, N \\
P &= P - \overline{m} D (\nabla \overline{u})^{sym} \\
q_u &= -D \nabla u.
\end{align*}
\]

Notice that there still appears only one transport coefficient, $D$. Also, note that since

\[
m = \sum_{i=1}^{N} m_i \quad \text{and} \quad q_M = \sum_{i=1}^{N} q_{M_i},
\]

one of the partial mass equations in the above may be replaced by the total mass equation,

\[
\frac{\partial m}{\partial t} = -\nabla \cdot (q_M + m \overline{u})
\]

with

\[
q_M = -D \nabla m.
\]

In this setting, the continuum velocity $\overline{v}$ is interpreted as a center of mechanical mass velocity, and in this center of mechanical mass frame, there is a non-zero total mass flux due to diffusion. Also, note that if the equilibrium thermodynamic pressure, $P$, may be expressed as a function of $u$ and $m$ only—as in the case of a homogeneous mixture—the $N - 1$ partial mass density equations may be uncoupled from the rest of the system, leaving formulation (48)/(70)-(72) derived for a single-component fluid. This means that homogeneous mixtures such as air may be treated in the same way as a single-component fluid.

Values for the Diffusion Transport Parameter

Here, measured sound propagation data is used together with formulas from §7.3 to compute the diffusion coefficient, $D$, of my formulation for various types
Table 1: diffusion parameters for various fluids at normal temperature and pressure

| fluid         | $D_0$ (m$^2$/s) | $D_{sd,0}$ (m$^2$/s) | $C_0$  |
|---------------|-----------------|----------------------|-------|
| gases         |                 |                      |       |
| helium        | $1.44 \times 10^{-4}$ | $1.82 \times 10^{-4}$ | 1.17  |
| neon          | $4.57 \times 10^{-5}$ | $5.25 \times 10^{-5}$ | 1.17  |
| argon         | $1.64 \times 10^{-5}$ | $1.84 \times 10^{-5}$ | 1.17  |
| krypton       | $8.77 \times 10^{-6}$ | $9.84 \times 10^{-6}$ | 1.17  |
| xenon         | $5.07 \times 10^{-6}$ | $5.76 \times 10^{-6}$ | 1.17  |
| nitrogen      | $2.01 \times 10^{-5}$ | $2.12 \times 10^{-5}$ (298 K) | 1.28  |
| oxygen        | $1.79 \times 10^{-5}$ | $2.32 \times 10^{-5}$ (298 K) | 1.12  |
| carbon dioxide| $1.08 \times 10^{-5}$ | $1.13 \times 10^{-5}$ (298 K) | 1.29  |
| methane       | $2.59 \times 10^{-5}$ | $2.40 \times 10^{-5}$ (298 K) | 1.51  |
| air           | $1.98 \times 10^{-5}$ |                      | 1.26  |
| liquids       |                 |                      |       |
| water         | $1.6 \times 10^{-6}$ (303 K) | $2.60 \times 10^{-9}$ (303 K) | 2.0 (303 K) |
| mercury       | $4.5 \times 10^{-7}$ (303 K) | $5.7 \times 10^{-9}$ (303 K) | 4.1 (303 K) |
| glycerol      | $5.4 \times 10^{-4}$ (298 K) | $1.9 \times 10^{-12}$ (298 K) | 0.78 (298 K) |
| benzene       | $4.8 \times 10^{-5}$ (298 K) | $2.2 \times 10^{-5}$ (298 K) | 70 (298 K) |
| ethyl alcohol | $1.9 \times 10^{-6}$ (298 K) | $1.4 \times 10^{-9}$ (298 K) | 1.4 (298 K) |
| castor oil    | $4.4 \times 10^{-4}$ (298 K) |                     | 0.43 (298 K) |

Some Values at Normal Temperature and Pressure

Table 1 provides values of the diffusion coefficient, $D_0$, and the self-diffusion coefficient, $D_{sd,0}$, (where available) for several gases and liquids at $T_0 = 300$ K (unless indicated otherwise) and $P_0 = 1.013 \times 10^5$ Pa. For the noble gases, helium, neon, argon, krypton, and xenon, $C_0$ is given by (127) and the diffusion coefficient is computed via (125) with shear viscosities from Kestin et al. [24] and mass densities determined by the classical ideal gas relationship,

$$m_0 = \frac{AP_0}{RT_0},$$

(307)

which is appropriate for each of the Table 1 gases in the normal temperature and pressure regime. For the diatomic gases, nitrogen and oxygen, and the polyatomic gases, carbon dioxide and methane, $D_0$ and $C_0$ are computed by equations (123) and (126), respectively, using data presented in Marques [30], viscosity data from Cole and Wakeham [11] and Trengrove and Wakeham [42], and densities computed via relation (307). For all [15] and the liquids, $D_0$ is

Note that even though air is a mixture of gases, mainly nitrogen and oxygen, we can treat it as though it were a single-component fluid as long as it remains a homogeneous mixture.

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computed via equation (117) and $C_0$ by relation (120). The sound propagation quantities, $\alpha/f^2$ and $c_0$, are calculated for air using $f = 11$ MHz and 0% humidity, given for mercury in Hunter et al. [22], and tabulated for the rest of the liquids in [53]. The viscosities and mass densities are taken from [52] for air, [54] for water, [22] for mercury, [51] for glycerol, [48] and [49] for benzene, [47] for ethyl alcohol, and [48] and [46] for castor oil. The self-diffusion coefficients are taken from Kestin et al. [24] for the noble gases, from Winn [44] for the diatomic and polyatomic gases, from Holz et al. [20] for water, from Nachtrieb and Petit [34] for mercury, from Tomlinson [41] for glycerol, from Kim and Lee [25] for benzene, and from Meckl and Zeidler [32] for ethyl alcohol.

From the values presented in Table 1, one makes the following observations.

• In each of the gases, the diffusion and self-diffusion coefficients are observed to be the same order of magnitude. However in liquids, the self-diffusion coefficients are several orders of magnitude smaller than the $D_0$ values. This indicates that although in gases the diffusion coefficient may be roughly approximated by self-diffusion, the same may not be said of liquids.

• The diffusion parameters of the noble gases are seen to decrease with increasing mass density.

• The value for $D_0$ in air is approximately a weighted average of the $D_0$ values for nitrogen and oxygen based on their fractional compositions in air ($\approx 0.8$ nitrogen and $\approx 0.2$ oxygen).

• With the exception of very light gases like helium and very heavy gases like krypton and xenon, diffusion coefficients for gases at normal temperature and pressure are typically on the order of $10^{-5}$ m$^2$/s.

• The $D_0$ values of water and ethyl alcohol—which fall into the category of medium viscosity, medium density liquids—are similar and on the order of $10^{-6}$ m$^2$/s, an order of magnitude smaller than that of a typical gas. The high viscosity, medium density liquids, glycerol and castor oil, possess similar $D_0$ values on the higher order of $10^{-4}$ m$^2$/s. Mercury’s viscosity is medium range like water and ethyl alcohol, but its higher mass density results in a smaller $D_0$ on the order of $10^{-7}$ m$^2$/s.

**Dependence on State Parameters**

**Gases** In general, it is observed from sound attenuation data for gases in the hydrodynamic regime that the product, $mD$, may vary with temperature but has negligible pressure or density dependence at a fixed temperature. Using this observation, together with relationship (73) and the fact that the Navier-Stokes shear viscosity $\eta_{NS}$ also has negligible pressure or density dependence,
leads us to conclude that although $C$ is possibly a function of $T$, it does not tend to vary much with $P$ or $m$ for gases. Typically, $\eta_{NS}$ may be expressed as a temperature power law of the form,

$$\eta_{NS} = \eta_{NS,r} \left( \frac{T}{T_r} \right)^\omega,$$

(308)

where $T_r$ is some reference temperature and $\eta_{NS,r}$ is the viscosity measured at $T_r$. Using this in equation (73), one finds

$$D(T,m) = \frac{\eta_{NS,r} C(T)}{m} \left( \frac{T}{T_r} \right)^\omega.$$

(309)

Equations (123) and (126) together imply

$$C_0 = \frac{1}{2} \left\{ \frac{\zeta_{NS,0}}{\eta_{NS,0}} + \left[ \frac{4}{3} + \left( 1 - \frac{1}{\gamma_0} \right) E\mu_0 \right] \right\}.$$

(310)

For noble gases, such as argon, one expects the values for $\zeta_{NS,0}$, $\gamma_0$, and $E\mu_0$ given in (124) to hold over a broad temperature range. Therefore, in the noble gases, we take $C = 7/6$ to be constant and, substituting this into (309),

$$D(T,m) = \frac{7}{6} \frac{\eta_{NS,r}}{m} \left( \frac{T}{T_r} \right)^\omega.$$

(311)

On the other hand, as observed in Tables 2-4, for non-monatomic gases such as air, nitrogen, and methane, $C$ displays a tendency to increase with temperature. In Tables 2-4, the $D_0$ values are computed by equation (117) with $\alpha/f^2$ calculated using [50] for air and taken from [36] for nitrogen and methane and with $c_0$ calculated from the classical ideal gas formula,

$$c_0 = \sqrt{\frac{\gamma_0 R T_0}{A}},$$

(312)

where the $\gamma_0$ values are taken from [52] for air and approximated to be constant over the studied temperature range for nitrogen and methane with respective values 1.4 and 1.3. The $C_0$ values appearing in Tables 2-4 are computed via equation (126) with Navier-Stokes shear viscosities taken from [52] for air and from [36] for nitrogen and methane and mass densities taken from [52] for air and computed by ideal gas formula (307) for nitrogen and methane.

**Liquids** Using equations (117) and (126) with sound speed and attenuation data from [53] and mass density and shear viscosity data from [54], one obtains the estimates of $D_0$ and $C_0$ for water at atmospheric pressure ($P_0 = 1.013 \times 10^5$ Pa) and various temperatures $T_0$ between the freezing and boiling point appearing in Table 5. As we can see, the parameter $C_0$ does not vary much over the entire temperature range, but the diffusion coefficient $D_0$ decreases
Table 2: diffusion coefficient for air at atmospheric pressure and various temperatures

| $T_0$ (K) | $D_0$ (m$^2$/s) | $C_0$ |
|-----------|-----------------|-------|
| 253       | $1.80 \times 10^{-5}$ | 1.22  |
| 263       | $1.83 \times 10^{-5}$ | 1.22  |
| 273       | $1.87 \times 10^{-5}$ | 1.24  |
| 283       | $1.90 \times 10^{-5}$ | 1.24  |
| 293       | $1.93 \times 10^{-5}$ | 1.25  |
| 303       | $1.97 \times 10^{-5}$ | 1.26  |
| 313       | $2.00 \times 10^{-5}$ | 1.27  |
| 323       | $2.03 \times 10^{-5}$ | 1.28  |

Table 3: diffusion coefficient for nitrogen gas at 0.01 atm and various temperatures

| $T_0$ (K) | $D_0$ (m$^2$/s) | $C_0$ |
|-----------|-----------------|-------|
| 77.1      | $1.37 \times 10^{-4}$ | 1.11  |
| 180       | $7.63 \times 10^{-4}$ | 1.22  |
| 260       | $1.57 \times 10^{-3}$ | 1.29  |
| 293       | $1.97 \times 10^{-3}$ | 1.31  |

Table 4: diffusion coefficient for methane gas at 0.01 atm and various temperatures

| $T_0$ (K) | $D_0$ (m$^2$/s) | $C_0$ |
|-----------|-----------------|-------|
| 77.1      | $1.58 \times 10^{-4}$ | 1.26  |
| 180       | $8.84 \times 10^{-4}$ | 1.36  |
| 260       | $1.92 \times 10^{-3}$ | 1.47  |
| 293       | $2.49 \times 10^{-3}$ | 1.52  |

Table 5: diffusion parameters for water at atmospheric pressure and various temperatures between the freezing and boiling point

| $T_0$ (K) | $D_0$ (m$^2$/s) | $D_{sd,0}$ (m$^2$/s) | $C_0$ |
|-----------|-----------------|----------------------|-------|
| 273       | $4.0 \times 10^{-6}$ | $1.10 \times 10^{-9}$ | 2.2   |
| 283       | $2.8 \times 10^{-6}$ | $1.53 \times 10^{-9}$ | 2.1   |
| 293       | $2.1 \times 10^{-6}$ | $2.02 \times 10^{-9}$ | 2.1   |
| 303       | $1.6 \times 10^{-6}$ | $2.59 \times 10^{-9}$ | 2.0   |
| 313       | $1.3 \times 10^{-6}$ | $3.24 \times 10^{-9}$ | 2.0   |
| 323       | $1.1 \times 10^{-6}$ | $3.96 \times 10^{-9}$ | 2.0   |
| 333       | $9.5 \times 10^{-7}$ | $4.75 \times 10^{-9}$ | 2.0   |
| 343       | $8.3 \times 10^{-7}$ | $5.62 \times 10^{-9}$ | 2.0   |
| 353       | $7.5 \times 10^{-7}$ | $6.56 \times 10^{-9}$ | 2.1   |
| 363       | $6.9 \times 10^{-7}$ | $7.57 \times 10^{-9}$ | 2.1   |
| 373       | $6.5 \times 10^{-7}$ | $8.67 \times 10^{-9}$ | 2.2   |
Table 6: diffusion coefficient for water at 273 K and 303 K and various pressures

| $T_0$ (K) | $D_0$ (m$^2$/s) | $C_0$ | $m_0D_0$ (kg/(m·s)) |
|-----------|-----------------|-------|---------------------|
| 273 K     |                 |       |                     |
| 9.81 × 10^4 | 4.03 × 10^-6   | 2.25  | 4.03 × 10^-3        |
| 4.90 × 10^4 | 3.96 × 10^-6   | 2.43  | 4.08 × 10^-3        |
| 9.81 × 10^4 | 3.85 × 10^-6   | 2.42  | 3.93 × 10^-3        |
| 1.47 × 10^8 | 3.59 × 10^-6   | 2.26  | 3.77 × 10^-3        |
| 1.96 × 10^8 | 3.39 × 10^-6   | 2.13  | 3.73 × 10^-3        |
| 303 K     |                 |       |                     |
| 9.81 × 10^4 | 1.61 × 10^-6   | 2.02  | 1.60 × 10^-3        |
| 4.90 × 10^4 | 1.58 × 10^-6   | 1.93  | 1.56 × 10^-3        |
| 9.81 × 10^4 | 1.52 × 10^-6   | 1.84  | 1.60 × 10^-3        |
| 1.47 × 10^8 | 1.52 × 10^-6   | 1.76  | 1.58 × 10^-3        |
| 1.96 × 10^8 | 1.54 × 10^-6   | 1.82  | 1.60 × 10^-3        |

with temperature. An excellent least squares fit is made to the Table 5 data with

$$D_0 = 3.9853 \times 10^{-7} \exp \left( \frac{3.5115 \times 10^{12}}{T_0^5} \right). \tag{313}$$

In the third column of Table 5, measured self-diffusion coefficients from Holz et al. [20] are tabulated for water at atmospheric pressure. Unlike our observation for gases, these self-diffusions are two to three orders of magnitude less than the corresponding $D_0$ values. Also, unlike $D_0$, the self-diffusion increases with temperature.

In Table 5, $D_0$ and $C_0$ are computed for water at two fixed temperatures, 273 K and 303 K, and various pressures roughly between 1 and 2000 atmospheres. The values are obtained using equations (117) and (126) together with data presented in Litovitz and Carnevale [29]. As we can see in the fourth column of Table 6, the product of the mass density and the diffusion coefficient does not vary much over the studied pressure range (8.96% for 273 K and 2.53% for 303 K). Therefore, as in gases, it is reasonable to assume that the quantity $mD$ is essentially pressure independent for water and perhaps for other liquids, as well, although this remains to be experimentally verified.

Using equations (117) and (126) with data from Hunter et al. [22] yields the estimates of $D_0$ and $C_0$ for liquid mercury at atmospheric pressure ($P_0 = 1.013 \times 10^5$ Pa) and various temperatures $T_0$ between 298 K and 403 K appearing in Table 7. Unlike our observation for water in Table 5, the $D_0$ values for mercury are seen to increase with increasing temperature. A fairly good fit to the Table 7 data is given by

$$D_0 = 1.12 \times 10^{-9} T_0^{1.05}. \tag{314}$$
Table 7: diffusion coefficient for liquid mercury at atmospheric pressure and various temperatures

| $T_0$ (K) | $D_0$ (m$^2$/s) | $C_0$ |
|-----------|-----------------|-------|
| 298       | $4.41 \times 10^{-7}$ | 3.90  |
| 303       | $4.46 \times 10^{-7}$ | 4.05  |
| 313       | $4.63 \times 10^{-7}$ | 4.31  |
| 318       | $4.76 \times 10^{-7}$ | 4.51  |
| 333       | $5.04 \times 10^{-7}$ | 5.01  |
| 338       | $5.15 \times 10^{-7}$ | 5.20  |
| 343       | $5.19 \times 10^{-7}$ | 5.32  |
| 353       | $5.34 \times 10^{-7}$ | 5.64  |
| 378       | $5.74 \times 10^{-7}$ | 6.27  |
| 403       | $6.10 \times 10^{-7}$ | 6.92  |

G List of Symbols

In addition to those introduced in §2, this paper utilizes the following symbols and notational conventions: 
the constants, 

- $R$ universal gas constant
- $k_B$ Boltzmann constant
- $A$ atomic weight
- $N_A$ Avagadro’s number,

the equilibrium thermodynamic quantities,

- $\tilde{s}(M)$ fundamental relation for entropy per mechanical mass
- $n_p$ particle number density
- $h(M)$ specific enthalpy
- $\alpha_P$ coefficient of thermal expansion
- $\kappa_T$ isothermal compressibility
- $c_V$ isochoric specific heat per mass
- $c_P$ isobaric specific heat per mass
- $\gamma$ ratio of specific heats, $c_P/c_V$
- $c$ adiabatic sound speed,

the non-equilibrium thermodynamic quantities,

- $j_A$ total $A$-flux
- $q_{A}^{\text{total}}$ non-convective $A$-flux
- $q_{A}^{\text{diff}}$ diffusion transport $A$-flux
- $r_A$ volumetric $A$-production/destruction rate
and

\[ \begin{align*}
\underline{P} & \quad \text{total pressure tensor} \\
\underline{P}_{\text{visc}} & \quad \text{viscous part of the pressure tensor} \\
\underline{P}_{\text{visc, s}} & \quad \text{spherical part of } \underline{P}_{\text{visc}} \\
f^{(M)} & \quad \text{external body force per mechanical mass} \\
q_{\text{heat}} & \quad \text{heat flux} \\
q_{\text{chem}} & \quad \text{energy flux due to chemical work},
\end{align*} \]

the transport coefficients,

\[ \begin{align*}
d_M, d_U & \quad \text{coefficients in general mass flux law} \\
\eta, \zeta & \quad \text{coefficients in general momentum flux law} \\
k_M, k_U & \quad \text{coefficients in general internal energy flux law}
\end{align*} \]

and

\[ \begin{align*}
\eta_{\text{NS}} & \quad \text{Navier-Stokes shear viscosity} \\
\zeta_{\text{NS}} & \quad \text{Navier-Stokes bulk viscosity} \\
k_F & \quad \text{Fourier heat conductivity} \\
D & \quad \text{my diffusion transport coefficient} \\
D_{sd} & \quad \text{self-diffusion coefficient},
\end{align*} \]

and the dimensionless parameters,

\[ \begin{align*}
Kn & \quad \text{Knudsen number} \\
Ma & \quad \text{Mach number} \\
\varepsilon & \quad \text{linearization parameter } \propto Ma \\
Eu & \quad \text{Euken ratio} \\
C & \quad \text{coefficient relating } D \text{ to } \eta_{\text{NS}}/m.
\end{align*} \]

Furthermore, the subscript ”0” is used to denote evaluation at the equilibrium state and the subscript ”1” to indicate first-order (linear) terms in the small \( \varepsilon \) expansion about equilibrium.

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