Abstract

§1 continues our discussion on interesting non-perfect gas effects. §2-§6 discusses non-equilibrium in energy modes—for example, rotational or vibrational non-equilibrium, showing that its impacts can be emulated by a bulk viscosity. Finally, in §7 we give some introduction to gas mixtures.

1 Normal Shock Relations Without Perfect Gas

Every compressible fluid mechanics text book has tables for normal shock relations, and explicit analytical formulas, under the perfect gas assumption. What happens when you do not have a perfect gas, but only a computer?

All agreed that it is just a question of how to do the computation. What follows is a good way to do it.

Let subscript $o$ denote upstream condition, while downstream conditions are unmarked. The three conservation laws are:

\begin{align*}
\rho u &= \rho_0 u_0 = \dot{m}_o, \\
p + \rho u^2 &= p_0 + \rho_0 u_0^2, \\
h + \frac{u^2}{2} &= h_o + \frac{u_0^2}{2}.
\end{align*}

1
It is instructive to eliminate velocity \( u \) and work only with thermodynamic state variables. It is straightforward to derive the following from (1), (2) and (3):

\[
h - h_o = \frac{1}{2}(p - p_o)\left(\frac{1}{\rho_o} + \frac{1}{\rho}\right), \quad (4)
\]

\[
p - p_o = -\dot{m}_o^2\left(\frac{1}{\rho} - \frac{1}{\rho_o}\right). \quad (5)
\]

Given a set of upstream thermodynamic state variables \((h_o, p_o, \rho_o, \ldots)\) and \(\dot{m}_o\), all possible downstream (post shock) thermodynamic variables \((\rho, T)\) can be obtained from the above two equations, provided appropriate equations of state are provided. For example, once the following representation of the equations of state is available:

\[
h = H(p, \rho). \quad (6)
\]

then it is straightforward to find from (4) the locus of all possible downstream conditions in the form of \(p(\rho; p_o, \rho_o, h_o)\) for arbitrary values of \(\dot{m}_o\). The function \(p(\rho; p_o, \rho_o, h_o)\) plotted on a \(p\) versus \(1/\rho\) diagram is called a Hugoniet curve. The resulting diagram is often called a Hugoniet Diagram. The solution for any specific \(\dot{m}_o\) is then obtained by the intersection of the straight line (always with negative slope) defined by (5) and the Hugoniet curve.

It is interesting to note that \(h\), the specific enthalpy, includes chemical energy. Thus, if chemical reactions occur between the upstream and downstream stations and chemical energy is released, this can be accounted for in respecting the fact that \(h\) includes “heat of formation” (energy) of its chemical components.

### 1.1 Some Properties of Hugoniet Diagrams

Consider a point on the Hugoniet curve \((p, 1/\rho)\), and consider an infinitesimal displacement along the Hugoniet curve (when the value of \(\dot{m}_o\) is changed infinitesimally). So, \(p\) goes to \(p + dp\) and \(1/\rho\) goes to \(1/\rho + d(1/\rho)\) (when \(\dot{m}_o\) goes to \(\dot{m}_o + d(\dot{m}_o)\)).

Taking the differential of (4), we have:

\[
dh = \frac{1}{2}(\frac{1}{\rho_o} + \frac{1}{\rho})dp + \frac{1}{2}(p - p_o)d(\frac{1}{\rho}). \quad (7)
\]
Now, substitute this into the differential equation of state \( Tds = dh - dp/\rho \), we obtain:

\[
Tds = \frac{1}{2} \left( \frac{1}{\rho_o} - \frac{1}{\rho} \right) dp + \frac{1}{2} (p - p_o) d\left(\frac{1}{\rho}\right).
\]

We are reminded that \( ds \) is the differential change of the downstream specific entropy when we move an infinitesimal amount (by changing \( m_o \)) along the Hugoniot curve. Using (5) to get rid of \( 1/\rho_o - 1/\rho \), we have:

\[
Tds = \frac{p - p_o}{2\rho_o^2} d\left(\frac{1}{\rho}\right) \left[ m_o^2 + \frac{dp}{d(1/\rho)} \right]
\]

where \( dp/d(1/\rho) \) is the slope of the Hugoniot curve at the point of interest. It is generally expected to be a negative number. The big square bracket of (9) is interesting: it sign depends on the relative magnitude of the slope of (5) and the slope of the local tangent to the Hugoniot curve.

The big deal coming out of all these manipulations is that \( ds = 0 \) whenever (5) “osculates” the Hugoniot curve. This osculating point is called the Chapman-Jouguet point, where it can easily be shown that the downstream condition is precisely sonic \( (\rho^2 = dp/d\rho) \) —note: this derivative-looking thing is locally the same as a partial derivative with \( s \) held constant). The Chapman-Jouguet point, as I assume you know, is most important in the theory of detonations.

The curvature of a curve is proportional to its second derivative. Thus, the curvature of a Hugoniot curve is proportional to \( \frac{d^2 p}{d(1/\rho)^2} \). The following are straightforward calculus manipulations:

\[
\frac{d^2 p}{d(1/\rho)^2} = \rho^2 \left( \frac{d}{dp} \rho^2 \left( \frac{dp}{d\rho} \right) \right) = \rho^4 \frac{d}{dp} \left( \frac{dp}{d\rho} \right) + 2\rho^3 \frac{dp}{d\rho}.
\]

At any osculating point of (5) and the Hugoniot curve, \( ds = 0 \), and \( dp/d\rho = a^2 \) where \( a \) is the isentropic speed of sound. Hence, at any osculating point, we have:

\[
\frac{d^2 p}{d(1/\rho)^2} = \rho^4 \frac{da^2}{d\rho} + 2\rho^3 a^2 = 2\rho^3 a^2 \left( \rho \frac{da}{a \ d\rho} + 1 \right) = 2\rho^2 a^2 \Gamma.
\]

It is seen that our old friend \( \Gamma \) —which is a state variable (or a constant)—is related to the curvature of the Hugoniot curve at osculating point(s). We shall discuss in class the potential for (non-perfect gas) complications for normal shock relations when \( \Gamma \) is not always positive.
2 Stress Tensor and Viscosity

The full Navier-Stokes stress tensor $\tau$ of a Newtonian fluid is:

$$
\tau_{i,j} = -p\delta_{i,j} + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \lambda \delta_{i,j} \frac{\partial u_k}{\partial x_k}, \quad (12)
$$

where $p$ is the “thermodynamic” pressure, $\mu$ is (dynamic) viscosity, and $\lambda$ is often called the second coefficient of viscosity. Of course, $\delta_{i,j}$ is the Kronecker Delta (equals to one when $i = j$, otherwise equals to zero), and Einstein’s summation convention is assumed. If the so-called Stokes postulate is adopted (that $p$ is the average of the three normal stresses of $\tau$), then $\lambda = -2\mu/3$.

The last term on the right hand side of (12) can be rewritten using the continuity equation to yield:

$$
\lambda \delta_{i,j} \frac{\partial u_k}{\partial x_k} = -\lambda \delta_{i,j} \frac{1}{\rho} \frac{D\rho}{Dt} \quad (13)
$$

where $D/Dt$ is the substantial derivative. It is thus seen that this term is only important for problems in which the density of the fluid changes rapidly with time—such as inside a shock wave or in very high frequency sound waves. In fact, experimental measurements of $\lambda$ nearly always come from measuring attenuation of high frequency sound waves.

3 Energy Relaxation and Bulk Viscosity

It is generally known that (rotational) energy relaxation can be related to “bulk viscosity” (viscous stresses that exist in the absence of shear). This note derives the analogy, displays the approximations involved, and shows that these two effects are not distinguishable by analyzing “low” frequency experimental sound attenuation data (how low is low?).

Consider a single (perfect) gas whose translational degree of freedom may not be in thermodynamic equilibrium with its internal degree of freedom (which shall be marked by an asterisk). Let $T$ be the translational temperature, and $T_*$ the temperature of the internal degree of freedom under scrutiny. For example, $T_*$ may be a “rotational temperature” or a “vibrational temperature.”
We assume the gas is a perfect gas and its (usual) equation of state is:

\[ p = \rho RT \]  

(14)

where \( R \) is the gas constant. The internal energy per unit mass of this gas is given by \( e + e_* \)—where \( e \) represents the translational (internal) energy (per unit mass), and is a state variable, while \( e_* \) is the internal energy which may not be in thermodynamic equilibrium—and thus is not a state variable. Assuming constant specific heats, we have

\[ e = C_v T, \quad h = C_p T, \quad (C_p - C_v = R), \quad e_* = C_* T_* \]  

(15)

where the notations are obvious. The first equation in (15) is the caloric equation of state. The last equation in (15) is actually a definition of \( T_* \).

4 The Governing Equations

The continuity equation is:

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0. \]  

(16)

We shall consider an “inviscid” formulation. The momentum equation is:

\[ \rho \frac{D\mathbf{V}}{Dt} = -\nabla p + \epsilon_1 \]  

(17)

where \( \epsilon_1 \) represents the neglected viscous term. The energy equation can be written as follows:

\[ \frac{D}{Dt} (C_p T + C_* T_* + \frac{\mathbf{V} \cdot \mathbf{V}}{2}) = \frac{1}{\rho} \frac{\partial p}{\partial t} + \epsilon_2, \]  

(18)

where \( \epsilon_2 \) represents the neglected heat conduction term. Equations (14) and (19) plus the above three conservation equations are the governing equations for the five unknowns, \( \mathbf{V}, p, \rho, T \) and \( T_* \).

Note that we have no difficulty in abandoning the thermodynamic equilibrium assumption so far.

In comparison to ordinary (full thermodynamic equilibrium) fluid mechanics, here we have one additional unknown, \( T_* \). We represent the energy relaxation process by a linear model:

\[ \frac{DT_*}{Dt} = \frac{T - T_*}{\tau} \]  

(19)
where the constant $\tau$ has the dimension of time. For rotational relaxation, $\tau$ is expected to be tens of collision times. For vibrational relaxation, $\tau$ is expected to be tens of thousands of collision times. Mathematically, it is easily seen that in the limit of asymptotically small $\tau$, we must have $T_* \approx T$. This is, in fact, what we tacitly assume in equilibrium fluid mechanics.

5 The linearized equations for sound propagation

Linearizing about a uniform quiescent state marked by subscript ‘$o$’ and using primes to mark the perturbations, we have ($V_o = 0$):

$$\frac{\partial p'}{\partial t} + \rho_o \nabla \cdot \mathbf{V}' = \epsilon_o,$$

$$\rho_o \frac{\partial \mathbf{V}'}{\partial t} = -\nabla p' + O(\epsilon_1),$$

$$C_p \frac{\partial T'}{\partial t} + C_* \frac{\partial T_*'}{\partial t} = \frac{1}{\rho_o} \frac{\partial p'}{\partial t} + O(\epsilon_2),$$

$$\frac{\partial T_*'}{\partial t} = \frac{T' - T_*'}{\tau} + O(\epsilon_3),$$

$$\frac{p'}{p_o} = \frac{\rho'}{\rho_o} + \frac{T'}{T_o} + \epsilon_4,$$

where $\epsilon_o$, $O(\epsilon_1) \ldots O(\epsilon_4)$ now include the neglected nonlinear terms. Note that (22) can be integrated with respect to time immediately, yielding:

$$C_p T' + C_* T_*' = \frac{1}{\rho_o} p' + O(\epsilon_2),$$

which will be used in place of (22).

6 The $\omega \tau << 1$ Case

Let $\omega$ represent the characteristic frequency of the problem. For example, in a problem of sound propagation, $\omega$ would be the frequency of the sound. Hence, the $\partial/\partial t$ operator is a $O(\omega)$ operator.

We now consider the case in the asymptotic limit of small $\omega \tau$. In the limit of $\omega \tau \to 0$, the “quasi-steady” approximation is the leading
approximation to (19):

\[ T_* \approx T + O(\omega \tau). \]  

(26)

In other words, the asterisked degrees of freedom is in equilibrium with all others (At this level of approximation, \( T_* \) is a state variable!).

The next approximation after (26) is:

\[ T_* = T - \tau \frac{DT_*}{Dt} \approx T - \tau \frac{DT}{Dt} + O(\omega \tau)^2. \]  

(27)

Note the substantial time derivative of \( T_* \) have been replaced by that of \( T \) (At this level of approximation, \( T_* \) is not a state variable. This is the level we shall work on).

6.0.1 Various Small \( \omega \tau \) Asymptotic Tricks

The linear version of (27) is obtained readily from (23):

\[ T'_* = T' - \tau \frac{\partial T'_*}{\partial t} + O(\epsilon_3) \approx T' - \tau \frac{\partial T'}{\partial t} + O(\epsilon_3, (\omega \tau)^2). \]  

(28)

This approximate relation can be used to eliminate \( T'_* \) completely from the remaining equations:

\[ \frac{\partial \rho'}{\partial t} + \rho_o \nabla \cdot \nabla' = \epsilon_o, \]  

(29)

\[ \rho_o \frac{\partial \nabla'}{\partial t} = -\nabla p' + O(\epsilon_1), \]  

(30)

\[ (C_p + C_s)T' - \frac{C_s \tau}{R} \frac{\partial T'}{\partial t} = \frac{1}{\rho_o} p' + O(\epsilon_2, \epsilon_3, (\omega \tau)^2), \]  

(31)

\[ \frac{p'}{\rho_o} = \frac{\rho'}{\rho_o} + \frac{T'}{T_o} + \epsilon_4. \]  

(32)

The question is: What does the framed energy relaxation term in (31) do to the propagation of sound waves? Obviously, when this term is absent, the solution is non-dissipative and sound waves propagate without attenuation.

Eliminating \( p' \) between (31) and (32), we have:

\[ \frac{\rho'}{\rho_o} = \left( \frac{C_p + C_s}{R} - 1 \right) \frac{T'_*}{T_o} - \frac{C_s \tau}{R T_o} \frac{\partial T'_*}{\partial t} + O(\epsilon_2, \epsilon_3, \epsilon_4, (\omega \tau)^2). \]  

(33)
When the term of order \( O(\omega \tau) \) (the unsteady term) is neglected, the leading approximation to (33) is:

\[
T' / T_0 = (\gamma_s - 1) \rho' / \rho_o + O(\omega \tau)
\] (34)

where

\[
\gamma_s \equiv \frac{C_p + C_*}{C_v + C_*}
\] (35)

the the ratio of specific heats of the gas in full equilibrium. Without degrading the accuracy of the analysis, we can use this leading approximate relation (34) to go back to (33) to eliminate the partial time derivative of \( T' \), yielding (with the help of (29)):

\[
\rho' \rho_o = -\gamma_s \frac{\rho'}{\rho_o} - \frac{C_* \tau (\gamma_s - 1)}{R \rho_o} (\nabla \cdot \mathbf{V}') + O(\epsilon_2, \epsilon_3, \epsilon_4, (\omega \tau)^2),
\] (36)

Solving for \( T' / T_0 \), we have:

\[
T' / T_0 = (\gamma_s - 1) \rho' / \rho_o - \frac{C_* \tau (\gamma_s - 1)^2}{R} (\nabla \cdot \mathbf{V}') + O(\epsilon_2, \epsilon_3, \epsilon_4, (\omega \tau)^2)
\] (38)

With the help of (32), we have:

\[
\frac{p'}{p_o} = \frac{\gamma'_s}{\gamma_s} \frac{\rho'}{\rho_o} - \frac{C_* \tau (\gamma_s - 1)^2}{R} (\nabla \cdot \mathbf{V}') + O(\epsilon_2, \epsilon_3, \epsilon_4, (\omega \tau)^2),
\] (39)

or

\[
p' = c_{os}^2 \rho' - \frac{p_o C_* \tau (\gamma_s - 1)^2}{R} (\nabla \cdot \mathbf{V}') + O(\epsilon_2, \epsilon_3, \epsilon_4, (\omega \tau)^2).
\] (40)

where \( c_{os} = \sqrt{\gamma_s p_o / \rho_0} \) is the equilibrium speed of sound.

6.0.2 The Punch Line

Using (40) in (30), we obtain:

\[
\rho_o \frac{\partial \mathbf{V}'}{\partial t} = -c_{os}^2 \nabla \rho' + \mu'' \nabla (\nabla \cdot \mathbf{V}') + O(\epsilon_2, \epsilon_3, \epsilon_4, (\omega \tau)^2),
\] (41)

where

\[
\mu'' = \frac{p_o C_* \tau (\gamma_s - 1)^2}{R}.
\] (42)
Most importantly, $\mu''$ does not depend on $\omega$. Equations (29) and (41) are the two governing equations for the two unknowns, $\rho'$ and $V'$. Equation (41) shows that to this order ($O(\omega\tau)^2$ terms neglected), the net effect of energy relaxation can be represented by an extra viscous force (with a finite effective bulk viscosity only and no ordinary viscosity) acting in a “barotropic” flow (i.e. $p' = c_o^2\rho'$).

Let $\mu_o$ denote the ordinary viscosity of the gas. We can write

$$\mu_o = O(\rho_o c_o \lambda)$$

(43)

where $\lambda$ can be interpreted as the ordinary mean-free-path of the gas. Hence, for fixed $C_o/R = O(1)$, we have:

$$\left| \frac{\mu''}{\mu} \right| = O\left( \frac{\rho_o \tau}{\rho_o c_o \lambda} \right) = O\left( \frac{c_o \tau}{\lambda} \right) = O\left( \frac{\tau}{\tau_{\text{collision}}} \right).$$

(44)

Since in general $\tau >> \tau_{\text{collision}}$, it thus appears that energy non-equilibrium can strongly influence the interpretation of bulk viscosity data.

### 6.1 Remarks

For any given gas (e.g. CO$_2$), $\tau$ is a material property, and depends on the thermodynamic state variables such as pressure and temperature (and of course, collision cross-sections of energy exchange collisions). The parameter $\omega\tau$ can change only as a consequence of changing $\omega$. It is seen that the manifestation of energy relaxation effect as an effective bulk viscosity is only valid for $\omega\tau << 1$. For sufficiently high frequency (i.e. when $\omega\tau$ is no longer small), the present theory must fail. In fact, when $\omega\tau$ is asymptotically large, the asterisked degree of freedom is expected to be “frozen,” and the flow becomes non-dissipative again. Thus the (energy relaxation-based) effective bulk viscosity should tend toward zero for asymptotically high frequencies. Hence, if the $\mu''$ experimentally determined using a bulk viscosity theory exhibits frequency dependences at very high frequencies, then energy relaxation may be playing a role.

If the experimentally determined $\mu$ exhibits no frequency dependence, there is no way one can attribute the separate roles played by the “real” and the “effective” bulk viscosity.

The question that provokes some soul searching is: when we attempt to include energy relaxation processes (read: chemical reactions) in deriving bulk viscosity, how can we be sure that we did not “double count” the impacts?
7 Mixture of gases

Consider a simple gas identified with subscript $n$. Its state variables are $\rho_n, T_n, p_n, e_n, h_n$ etc.

The following differential equation of state holds:

$$T_n ds_n = dh_n - \frac{dp_n}{\rho_n}. \quad (45)$$

Or, multiplying through by $\rho_n$, we have:

$$\rho_n T_n ds_n = \rho_n dh_n - dp_n. \quad (46)$$

Now, consider a mixture of $N$ distinct simple gases at a single temperature $T$. Now what is the appropriate differential equation of state for the mixture?

7.1 State variables for a mixture

The definition of the density $\rho$ of the mixture is straightforward:

$$\rho = \sum_{n=1}^{N} \rho_n. \quad (47)$$

We shall denote the mass fraction of each of the components by $X_n$:

$$X_n \equiv \frac{\rho_n}{\rho}. \quad (48)$$

Note that $\sum_{n=1}^{N} X_n = 1$ by definition.

The definition of the pressure $p$ of the mixture is straightforward:

$$p = \sum_{n=1}^{N} p_n. \quad (49)$$

The definition of the specific enthalpy $h$ and specific entropy $s$ of the mixture are handled differently, but straightforward:

$$h = \frac{1}{\rho} \sum_{n=1}^{N} \rho_n h_n = \sum_{n=1}^{N} X_n h_n, \quad (50)$$

$$s = \frac{1}{\rho} \sum_{n=1}^{N} \rho_n s_n = \sum_{n=1}^{N} X_n s_n. \quad (51)$$
Now we look for the appropriate differential equation of state relating the above.

It should be obvious to you that we need more than two state variables to define the state of the mixture. In addition to $\rho, T$ (for example), we need $X_1, X_2, \ldots, X_n$.

### 7.2 Duham-Gibbs Equation

Summing (46) over all $N$ species with $T_n = T$, we obtain:

\[
\rho T ds = \rho dh - dp - \rho \sum_{n=1}^{N} \mu_n dX_n
\]  \hspace{1cm} (52)

where $\mu_n$ (it is not viscosity; but the symbol $\mu$ is commonly used to represent it) is called the chemical potential of the $n$-th component, defined by:

\[
\mu_n = h_n - T s_n.
\]  \hspace{1cm} (53)

Dividing (52) by $\rho$, we have:

\[
T ds = dh - \frac{dp}{\rho} - \sum_{n=1}^{N} \mu_n dX_n
\]  \hspace{1cm} (54)

which is the famed Duham-Gibbs equation. It is the differential equation of state for mixtures.

### 8 Homeworks

1. For a perfect gas, $H(p, \rho)$ as introduced by (6) would be $(C_p/R)(p/\rho)$. Find the Hugoniot curve for constant $C_p/R = \gamma/(\gamma-1)$. Sketch the Hugoniet curve.

2. Consider a very strong shock such that $p_1$ is negligible compared to $p_2$, and $h_1$ is negligible compared to $h_2$. Find $\rho_2/\rho_1$ in this strong shock limit.

3. What happens if some chemical reaction happens when the shock is strong, and some chemical energy is released? Sketch what you think would happen to the Hugoniet curve.

4. Mess around with the full governing equations in §3, neglecting $\epsilon_1$ and $\epsilon_2$, and try to get a single scalar equation which does
not contain \( V \). Using the perfect gas equation of state, can you integrate this equation (a) when \( \tau = 0 \), and (b) when \( \tau = \infty \)? How would you related what you found with traditional concept of entropy for the two limiting cases? How big \( \tau \) needs to be in order for you to conclude that \( \tau = \infty \) is a good approximation for your problem?

5. On the energy relaxation/bulk viscosity analysis: how difficult is it to remove the perfect gas assumption? Do you then care what \( \Gamma_o \) is?

6. Suppose we are interested in rotational energy relaxation of diatomic gases. What would be your guess of \( C_\ast / R \)?

7. Now you have been working with air which is a mixture of many simple gases. How come you never need to worry about the last term in (54)? If your gas mixture is chemically reacting, under what condition can you neglect the last term?