

Mixtures of Maxwell Molecules

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The linearized collision integrals for mixtures of Maxwell molecules are considered. A simple proof of the eigentheory is given. Relations for and amongst eigenvalues are obtained. A brief discussion of the corresponding relaxation theory is also included.

1. INTRODUCTION

IN a pioneering paper, Wang Chang and Uhlenbeck¹ proved that a certain complete set of polynomials are eigenfunctions of the linearized collision integral for Maxwell molecules. The corresponding analysis for mixtures of Maxwell molecules was not given until much later.² (In earlier treatments, Curtiss³ implicitly considers the eigentheory for isotropic distribution functions and Naze^{4,5} considers only one portion of the collision operator.) In this note, expressions for the eigenvalues are obtained as well as relations amongst them. In the course of the discussion a very simple proof for the eigentheory of Maxwell molecules is given. As an application the relaxation theory is considered.

2. EIGENTHEORY

A typical collision term for a multicomponent gas is

$$J(f_\alpha, f_\beta) = \int (f'_\alpha f'_\beta - f_\alpha f_\beta) B^{\alpha\beta} \cdot (\theta, |\xi_\alpha - \xi_\beta|) d\theta d\epsilon d\xi_\beta. \quad (1)$$

This represents β -gas collisions in the α -gas equation. In (1) and in what follows, the notation is standard and no explanation is deemed necessary. We introduce mean local Maxwellian distributions

$$f_{0l} = n_l (m_l / 2\pi kT)^{3/2} e^{-m_l(\xi_l - \mathbf{u})^2 / 2kT}; \quad l = \alpha, \beta. \quad (2)$$

The number densities n_α, n_β , the mean velocity \mathbf{u} , and the mean temperature T may all be regarded as functions of space and time.

¹ C. S. Wang Chang and G. E. Uhlenbeck, University of Michigan Engineering Report Project M999 (1954). See also L. Waldmann, in *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1958), Vol. 12.

² L. Sirovich, *Phys. Fluids* 5, 903 (1962) (see Appendix A).

³ C. F. Curtiss, University of Michigan Department of Chemistry Report NSF-2746 (1957).

⁴ J. Naze, *Compt. Rend.* 251, 651 (1960).

⁵ J. Naze, *Compt. Rend.* 251, 854 (1960).

Linearizing (1) about the local Maxwellians (2), we obtain

$$J_{\alpha\beta} \sim L_{\alpha\beta} = \int f_{0\alpha} f_{0\beta} (g'_\alpha + g'_\beta - g_\alpha - g_\beta) B^{\alpha\beta} d\theta d\epsilon d\xi_\beta,$$

where

$$g_l = (f - f_{0l}) / f_{0l}; \quad l = \alpha, \beta.$$

Introducing the following normalization and notation:

$$\begin{aligned} \zeta &= (\xi_\alpha - \mathbf{u})(m_\alpha / kT)^{1/2}, \\ \mathbf{n} &= (\xi_\beta - \mathbf{u})(m_\beta / kT)^{1/2}, \\ \omega(x) &= (2\pi)^{-3/2} e^{-x^2/2}, \end{aligned} \quad (3)$$

we can write

$$L_{\alpha\beta} = f_{0\alpha} n_\beta (M^\alpha g_\alpha + N^\alpha g_\beta) \quad (4)$$

with

$$M^\alpha \varphi = \int \omega(\eta) [\varphi(\zeta') - \varphi(\zeta)] B^{\alpha\beta} d\theta d\epsilon d\mathbf{n}, \quad (5)$$

$$N^\alpha \varphi = \int \omega(\eta) [\varphi(\mathbf{n}') - \varphi(\mathbf{n})] B^{\alpha\beta} d\theta d\epsilon d\mathbf{n}. \quad (6)$$

We use the superscript α to indicate that M^α, N^α arise in the α -gas equation. In the β -gas equation the analogous terms are written M^β, N^β and integration is then with respect to ζ . Naze^{4,5} considers only the operator M .

The collision transformation for velocities, under the normalization (3), becomes

$$\begin{aligned} \zeta' &= \zeta - [2m_\beta / (m_\beta + m_\alpha)] [\zeta - (m_\alpha / m_\beta)^{1/2} \mathbf{n}] \cdot \mathbf{k} \mathbf{k}, \\ \mathbf{n}' &= \mathbf{n} - [2m_\alpha / (m_\alpha + m_\beta)] [\mathbf{n} - (m_\beta / m_\alpha)^{1/2} \zeta] \cdot \mathbf{k} \mathbf{k}, \end{aligned} \quad (7)$$

where $\mathbf{k} = \mathbf{k}(\theta, \epsilon)$ is the unit vector in the apse direction.

Define the inner product

$$(\psi, \varphi) = \int \psi^*(\mathbf{x}) \varphi(\mathbf{x}) \omega(\mathbf{x}) d\mathbf{x},$$

where the asterisk denotes the complex conjugate. By standard arguments, one has

$$\begin{aligned}
 (\psi, M^\alpha \varphi) &= \int \omega(\zeta)\omega(\mathbf{n})\psi^*(\zeta) \\
 &\quad \cdot [\varphi(\zeta') - \varphi(\zeta)]B^{\alpha\beta} d\theta d\epsilon d\mathbf{n} d\zeta \\
 &= -\frac{1}{2} \int \omega(\zeta)\omega(\mathbf{n})[\psi^*(\zeta') - \psi^*(\zeta)] \\
 &\quad \cdot [\varphi(\zeta') - \varphi(\zeta)]B^{\alpha\beta} d\theta d\epsilon d\mathbf{n} d\zeta \\
 &= \int \omega(\zeta)\omega(\mathbf{n})\varphi(\zeta) \\
 &\quad \cdot [\psi^*(\zeta') - \psi^*(\zeta)]B^{\alpha\beta} d\theta d\epsilon d\mathbf{n} d\zeta, \tag{8}
 \end{aligned}$$

$$\begin{aligned}
 (\psi, N^\alpha \varphi) &= \int \omega(\zeta)\omega(\mathbf{n})\psi^*(\zeta) \\
 &\quad \cdot [\varphi(\mathbf{n}') - \varphi(\mathbf{n})]B^{\alpha\beta} d\theta d\theta d\zeta d\mathbf{n} \\
 &= -\frac{1}{2} \int \omega(\zeta)\omega(\mathbf{n})[\psi^*(\zeta) - \psi^*(\zeta)] \\
 &\quad \cdot [\varphi(\mathbf{n}') - \varphi(\mathbf{n})]B^{\alpha\beta} d\theta d\epsilon d\zeta d\mathbf{n} \\
 &= \int \omega(\zeta)\omega(\mathbf{n})\varphi(\mathbf{n}) \\
 &\quad \cdot [\psi^*(\zeta') - \psi^*(\zeta)]B^{\alpha\beta} d\theta d\epsilon d\zeta d\mathbf{n}. \tag{9}
 \end{aligned}$$

The operators M^α and N^α are isotropic, and hence for functions of the form $g(|x|)Y_{lm}(\varphi, \chi)$,

$$\begin{aligned}
 M^\alpha g(|x|)Y_{lm} &= \tilde{g}(|x|)Y_{lm}, \\
 N^\alpha g(|x|)Y_{lm} &= \tilde{\tilde{g}}(|x|)Y_{lm}; \tag{10}
 \end{aligned}$$

i.e., the spherical harmonics

$$Y_{lm} = P_n^m(\cos \varphi)e^{im\chi}$$

are characteristic. (φ, χ should be regarded as polar angles with respect to a fixed frame.)

Next we introduce the Sonine polynomials

$$S_m^n(x) = \{(-)^n/n!\}(d/ds^n)[(1-s)^{m+n}e^{sx}]_{s=0},$$

and from these the functions^{1,6}

$$\psi_{rlm} = S_{l+1}^r(\frac{1}{2}\eta^2)\eta^l P_l^m(\cos \varphi)e^{im\chi},$$

which are polynomials of degree $2r + l$. This complete set of functions has the orthogonality property

$$\begin{aligned}
 (\psi_{r'l'm'}, \psi_{rlm}) &= \frac{2^{l+1}\Gamma(r+l+\frac{3}{2})}{\pi^{\frac{3}{2}}r!(2l+1)} \frac{(l+|m|)!}{(l-|m|)!} \delta_{rr'} \delta_{ll'} \delta_{mm'} \\
 &= N^{rlm} \delta_{rr'} \delta_{ll'} \delta_{mm'}. \tag{11}
 \end{aligned}$$

⁶H. M. Mott-Smith, Massachusetts Institute of Technology, Lincoln Laboratory Report V-2 (1954).

We now restrict attention to force laws for which

$$B^{\alpha\beta} = B^{\alpha\beta}(\theta), \tag{12}$$

which is true for Maxwell molecules. Substituting (7) in $M^\alpha \psi_{rlm}$ and $N^\alpha \psi_{rlm}$, we see that each of these is a polynomial in ζ of degree $\leq 2r + l$. From the orthogonality of the polynomials, (11), we see that $(\psi_{r'l'm'}, M^\alpha \psi_{rlm})$ and $(\psi_{r'l'm'}, N^\alpha \psi_{rlm})$ are zero for $2r' + l' > 2r + l$. But from the last lines of (8) and (9), these expressions are zero unless $2r + l > 2r' + l'$. From (13), however, these expressions vanish unless $m = m'$ and $l = l'$ and therefore unless $r = r'$. This proves therefore that for intermolecular force laws such that (12), then

$$\begin{aligned}
 M^\alpha \psi_{rlm}(\zeta) &= \int \omega(\mathbf{n})[\psi_{rlm}(\zeta') - \psi_{rlm}(\zeta)]B^{\alpha\beta}(\theta) d\epsilon d\theta d\mathbf{n} \\
 &= \mu_{ri}^\alpha \psi_{rlm}(\zeta), \\
 N^\alpha \psi_{rlm}(\mathbf{n}) &= \int \omega(\eta)[\psi_{rlm}(\mathbf{n}') - \psi_{rlm}(\mathbf{n})]B^{\alpha\beta}(\theta) d\epsilon d\theta d\mathbf{n} \\
 &= \nu_{ri}^\alpha \psi_{rlm}(\zeta).
 \end{aligned}$$

The eigenvalues $\mu_{ri}^\alpha, \nu_{ri}^\alpha$ do not depend on the subscript m since M and N commute with the rotation operator. It is important to note that N^α transforms a β -gas polynomial $\psi_{rlm}(\mathbf{n})$ into an α -gas polynomial $\psi_{rlm}(\zeta)$. We note in passing that the simple gas eigentheory follows from the above by setting $m_\alpha = m_\beta$, since $(M + N)$ is then the simple gas linearized collision operator.

To obtain explicit expressions for μ_{ri}, ν_{ri} , it suffices to suppress m , and on taking inner products we obtain

$$\mu_{ri}^\alpha = \frac{1}{N^{ri}} \int \omega(\zeta)\psi_{ri}(\zeta) \left[\int \omega(\mathbf{n}) \left(\int B^{\alpha\beta}(\theta)[\psi_{ri}(\zeta') - \psi_{ri}(\zeta)] d\epsilon d\theta \right) d\mathbf{n} \right] d\zeta, \tag{13}$$

$$\nu_{ri}^\alpha = \frac{1}{N^{ri}} \int \omega(\zeta)\psi_{ri}(\zeta) \left[\int \omega(\mathbf{n}) \left(\int B^{\alpha\beta}(\theta)[\psi_{ri}(\mathbf{n}') - \psi_{ri}(\mathbf{n})] d\epsilon d\theta \right) d\mathbf{n} \right] d\zeta. \tag{14}$$

The reduction of these expressions can be accomplished very simply by noting several features of the calculation. In (13) and (14) the expressions in the large parentheses are polynomials in \mathbf{n} and ζ . Furthermore, by orthogonality (11), only the $2r + l$ power of \mathbf{n} need be retained from the large-square-

bracket expression in carrying out the ζ integration. These terms, however, are of the zeroth power in \mathbf{n} . Therefore in evaluating $\psi_{r,l}(\mathbf{n}')$ and $\psi_{r,l}(\zeta')$ in (13) and (14) we may suppress all powers of ζ less than $2r + l$ and also take the limit $\eta \rightarrow 0$.

We write

$$\mathbf{k} \cdot [\zeta - (m_\alpha/m_\beta)^{1/2} \mathbf{n}] = |\zeta - (m_\alpha/m_\beta)^{1/2} \mathbf{n}| \cos \theta.$$

The polar direction of the fixed reference frame is denoted by \mathbf{i} . $\psi_{r,l}$ may be then written as

$$\psi_{r,l}(\mathbf{n}) = S_{l+\frac{1}{2}}^r(\frac{1}{2}\eta^2) |\mathbf{n}|^l P_l[(\mathbf{i} \cdot \mathbf{n})/|\eta|],$$

also

$$\psi_{r,l}(\mathbf{n}') = S_{l+\frac{1}{2}}^r(\frac{1}{2}\eta'^2) |\mathbf{n}'|^l P_l[(\mathbf{i} \cdot \mathbf{n}')/|\mathbf{n}'|].$$

Making use of the remarks of the previous paragraph, we obtain

$$\begin{aligned} \nu_{r,l}^\alpha &= \frac{1}{N^{r,l}} \int \omega(\zeta) \psi_{r,l}(\zeta) \left(\int \omega(\mathbf{n}) \left\{ \int B^{\alpha\beta}(\theta) \left[S_{l+\frac{1}{2}}^r(\frac{1}{2}\eta^2) \right. \right. \right. \\ &\quad \cdot |\mathbf{n}'|^l P_l\left(\frac{\mathbf{i} \cdot \eta'}{|\mathbf{n}'|}\right) - \delta_{r,0} \delta_{l,0} \left. \right\} d\epsilon d\theta \left. \right) d\mathbf{n} \left. \right) d\zeta \\ &= \frac{1}{N^{r,l}} \int \omega(\zeta) \psi_{r,l}(\zeta) \left(\int \omega(\mathbf{n}) \left\{ \int B^{\alpha\beta}(\theta) \right. \right. \\ &\quad \cdot \left[S_{l+\frac{1}{2}}^r \left(\frac{4m_\alpha m_\beta}{(m_\alpha + m_\beta)^2} \frac{\zeta^2}{2} \right) \zeta^l \frac{2(m_\alpha m_\beta)^{1/2}}{m_\alpha + m_\beta} \right. \\ &\quad \cdot \cos^l \theta \cdot P_l(\mathbf{i} \cdot \mathbf{k}) - \delta_{r,0} \delta_{l,0} \left. \right] d\epsilon d\theta \left. \right) d\mathbf{n} \left. \right) d\zeta \\ &= 2\pi \left(\frac{2(m_\alpha m_\beta)^{1/2}}{m_\alpha + m_\beta} \right)^{2r+l} \int_0^{\pi/2} B^{\alpha\beta}(\theta) \\ &\quad \cdot [\cos^{2r+l} \theta P_l(\cos \theta) - \delta_{r,0} \delta_{l,0}] d\theta, \end{aligned} \tag{15}$$

where we have briefly indicated the steps in the calculation. (Note that $\nu_{r,l}^\alpha = \nu_{r,l}^\beta$, and we may therefore suppress the superscript.) In going to the last form of (15), the addition theorem of spherical harmonics has been used. In the same way we also find that (Naze⁵ has previously obtained this expression)

$$\begin{aligned} \mu_{r,l}^\alpha &= 2\pi \int_0^{\pi/2} B^{\alpha\beta}(\theta) \left[\left(1 - \frac{4m_\alpha m_\beta}{(m_\alpha + m_\beta)^2} \cos^2 \theta \right)^{r+l/2} \right. \\ &\quad \cdot P_l \left(\frac{1 - [2m_\beta/(m_\alpha + m_\beta)] \cos^2 \theta}{\{1 - [4m_\alpha m_\beta/(m_\alpha + m_\beta)^2] \cos^2 \theta\}^{1/2}} \right) - 1 \left. \right] d\theta. \end{aligned} \tag{16}$$

The simple gas eigenvalue, $\lambda_{r,l}$, is obtained by setting $m_\alpha = m_\beta$ and adding $\mu_{r,l}$ to $\nu_{r,l}^{(1)}$,

$$\begin{aligned} \lambda_{r,l} &= 2\pi \int_0^{\pi/2} B(\theta) [\cos^{2r+l} \theta P_l(\cos \theta) \\ &\quad + \sin^{2r+l} \theta P_l(\sin \theta) - 1 - \delta_{r,0} \delta_{l,0}] d\theta. \end{aligned} \tag{17}$$

Since the "cross section" $B^{\alpha\beta}$ is positive, one has by inspection

$$\begin{aligned} \nu_{0,0} &= 0, \\ \nu_{r,0} &> \nu_{m,0} \geq 0, \quad \text{for } m > r > 0, \\ \nu_{r,0} &> \nu_{r,l}, \\ \nu_{r,l} &\rightarrow 0, \quad |r + l| \rightarrow \infty; \end{aligned} \tag{18}$$

$$\begin{aligned} \mu_{0,0} &= 0, \\ \mu_{r,l} &< 0, \quad r \text{ or } l \neq 0, \\ \mu_{r,0} &> \mu_{m,0}, \quad m > r > 0, \\ \mu_{r,0} &> \mu_{r,l}. \end{aligned} \tag{19}$$

A relation between cross-collisional eigenvalues can be obtained. Let x, y denote two arbitrary real quantities and consider

$$\begin{aligned} n_\beta(x^2 \mu_{r,l}^\alpha + xy \nu_{r,l}) + n_\alpha(y^2 \mu_{r,l}^\beta + xy \nu_{r,l}) \\ = n_\beta[x\psi_{r,l}(\eta), M^\alpha x\psi_{r,l}(\zeta)] + n_\beta[x\psi_{r,l}(\zeta), N^\alpha y\psi_{r,l}(\eta)] \\ + n_\alpha[y\psi_{r,l}(\zeta), M^\beta y\psi_{r,l}(\eta)] + n_\alpha[y\psi_{r,l}(\zeta), N^\beta x\psi_{r,l}(\zeta')] \\ = -\frac{1}{2} \int [x\psi_{r,l}(\zeta) + y\psi_{r,l}(\eta) - x\psi_{r,l}(\zeta') \\ - y\psi_{r,l}(\eta')]^2 B^{\alpha\beta}(\theta) d\epsilon d\theta d\mathbf{n} d\zeta \leq 0. \end{aligned} \tag{20}$$

Strict inequality is obtained in (20) for $rl \neq (0, 0), (1, 0), (0, 1)$. From (20) we obtain

$$\frac{n_\alpha + n_\beta}{2(n_\alpha n_\beta)^{1/2}} \nu_{r,l} \leq (\mu_{r,l}^\alpha \mu_{r,l}^\beta)^{1/2}. \tag{21}$$

A weaker form of this is

$$(\mu_{r,l}^\alpha \mu_{r,l}^\beta)^{1/2} \geq \nu_{r,l}. \tag{22}$$

Strict inequality holds in (21) and (22) under the conditions stated below (20). As is well known, $B^{\alpha\beta}(\theta)$ for Maxwell molecules diverges at $\theta = \frac{1}{2}\pi$ as $\cos^{-1}\theta$, and hence the expressions (15), (16) are conditionally convergent. In particular, $\mu_{r,l} \rightarrow -\infty$ as $|r + l| \rightarrow \infty$. On applying (18) and (19) to (17), we recover known properties of the eigenvalues $\lambda_{r,l}$.

3. RELAXATION OF A BINARY GAS

In order to apply the results of the last section, we consider a homogeneous binary mixture of Maxwell molecules. The linearized equations are

$$\partial g/\partial t = n_\alpha L^\alpha g_\alpha + n_\beta M^\alpha g_\alpha + n_\beta N^\alpha g_\beta, \tag{23}$$

$$\partial g_\beta/\partial t = n_\beta L^\beta g_\beta + n_\alpha M^\beta g_\beta + n_\alpha N^\beta g_\alpha, \tag{24}$$

where L is the one-component linearized collision operator. Taking the inner product of (23) with

$\psi_{rim}(\zeta)$ and (24) with $\psi_{rim}(\mathbf{n})$, we obtain

$$\frac{\partial}{\partial t} \begin{bmatrix} a_{rim}^\alpha \\ a_{rim}^\beta \end{bmatrix} = \begin{bmatrix} n_\alpha \lambda_{ri}^\alpha + n_\beta \mu_{ri}^\alpha & n_\beta \nu_{ri} \\ n_\alpha \nu_{ri} & n_\beta \lambda_{ri}^\beta + n_\alpha \mu_{ri}^\beta \end{bmatrix} \begin{bmatrix} a_{rim}^\alpha \\ a_{rim}^\beta \end{bmatrix}, \quad (25)$$

where

$$a_{rim} = (1/N^{rim})(\psi_{rim}, g).$$

(Curtiss⁸ considers the case $l = m = 0$.) Using (22) one easily shows that (25) leads to only exponentially decaying solutions. This may, however, be demonstrated more generally by forming the norm from the inner product defined below (7),

$$\|g\| = (g, g)^{\frac{1}{2}}.$$

We then easily obtain

$$(\partial/\partial t) \|g\| < \lambda \|g\| < 0, \quad (26)$$

where λ is easily estimated from the eigenvalues. The inequality follows from well-known integral relations [see (8) and (9)]. In fact (26) is the linearized form of the H theorem.

Various limiting situations of (25) may be discussed on the basis of (15), (16), and (17). This is straightforward, and we do not carry out such a discussion, especially since special cases are to be found in the literature.^{2,3,7}

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⁷ T. F. Morse, *Phys. Fluids* **6**, 1420 (1963).