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Louis Biolsi Jr.
*Missouri University of Science and Technology*, biolsi@mst.edu



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# Effect of angular momentum on the relaxation time in a multicomponent gas mixture

Louis Biolsi

*Department of Chemistry, University of Missouri–Rolla, Rolla, Missouri 65401*
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The effects of molecular angular momentum (spin polarization) on the bulk viscosity and relaxation time in a multicomponent gas mixture are considered. Formal theoretical results are obtained, using the Wang Chang–Uhlenbeck approach to the kinetic theory of gases with internal states. The results are given in terms of integrals over the weighted quantum mechanical degeneracy averaged cross section.

The kinetic theory of a single component polyatomic gas was developed by Wang Chang and Uhlenbeck[1] and extended to gas mixtures by Monchick, Yun, and Mason.[2] Since molecules possess rotational degrees of freedom, there are two independent vector quantities associated with the transport properties; the linear momentum and the angular momentum.[3] Contributions to the transport properties due to their dependence on the angular momentum vector are called spin polarization effects. These effects account for the polarization of molecular angular momentum caused by the partial alignment of the angular momentum vectors of the rotating molecules owing to gradients in the gas.[4]

McCourt and Snider[5] developed a formal quantum mechanical approach to the spin polarization effect on thermal conductivity for a single-component polyatomic gas. Formal quantum mechanical results for the spin polarization effect on thermal conductivity in a polyatomic gas mixture at uniform composition[6] and in a steady state[7] and on thermal diffusion[7] have also been obtained.

Classical model calculations[4,8] indicate that spin polarization contributes significantly to transport properties, such as thermal conductivity and thermal diffusion, that depend sensitively on inelastic collisions. Relaxation times in dilute polyatomic gases depend only on inelastic collision processes and should exhibit a spin polarization effect. Thus the purpose of this paper is to obtain expressions for the spin polarization effect on rotational relaxation times, using the Wang Chang–Uhlenbeck approach[1] to kinetic theory.

## I. THE SEMICLASSICAL BOLTZMANN EQUATION

The kinetic equation solved by Wang Chang and Uhlenbeck is[1]

$$\frac{\partial f_{qi}}{\partial t}+\mathbf{v}_q\cdot\frac{\partial}{\partial \mathbf{r}}f_{qi}=\sum_{q'}\sum_{jkl}\int\cdots\int(f'_{qk}f'_{1q'l}-f_{qi}f_{1q'j})\times gI^{kl}_{ij}(g,\chi,\phi)\sin\chi\,d\chi\,d\phi\,d\mathbf{v}_{1q'}\;,\quad(1)$$

where $f_{qi}$ is the singlet distribution function, $E_{qi}$ is the internal energy of the $q$th chemical species in internal quantum state $i$, and $I^{kl}_{ij}(g,\chi,\phi)$ is the differential scattering cross section for the process in which molecules $q$ and $q'$, initially in internal states $i$ and $j$, respectively, go to final internal states $k$ and $l$, respectively. The primes denote postcollision values and $\mathbf{g}$ is the initial relative velocity. Equation (1) is called the semiclassical Boltzmann equation because the translational motion is treated classically and the internal motion is treated quantum mechanically.

Equation (1) has been obtained by assuming the existence of symmetry between inverse processes. However such symmetry exists only if the internal states are nondegenerate or if the cross section is degeneracy averaged.[6] Since the primary motivation for this work is to examine rotational relaxation times and, since rotational states are degenerate, the degeneracy averaged cross section will be used. Degeneracy averaging does not appear to wash out spin polarization effects since loaded spheres have inverse collisions but show a definite spin polarization effect.[4,8]

The Boltzmann equation is solved by a perturbation technique. The distribution function is written as

$$f_{qi}=f^{\circ}_{qi}(1+\Phi_{qi}+\cdots)\;,\quad(2)$$

where $f^{\circ}_{qi}$ is the equilibrium solution of the Boltzmann equation and $\Phi_{qi}$ is the perturbation function. For a system of rotating polyatomic molecules with zero net macroscopic angular momentum and zero average internal angular momentum[6]

$$f^{\circ}_{qi}=\frac{n_q}{Q_q}\left(\frac{m_q}{2\pi kT}\right)^{3/2}e^{-(W_q^2+\epsilon_{qi})}\;,\quad(3)$$

where

$$\mathbf{W}_q=\sqrt{\frac{m_q}{2kT}}\,\mathbf{V}_q\;,\quad \epsilon_{qi}=\frac{E_{qi}}{kT}\;,\quad Q_q=\sum_i e^{-\epsilon_{qi}}\;,$$

and

$$\mathbf{V}_q=\mathbf{v}_q-\mathbf{v}_0\;,$$

where $\mathbf{v}_0$ is the mass-average velocity.

The set of integral equations for $\Phi_{qi}$ is given by Eq. (18) in Ref. 6. The form of this set of integral equations suggests that $\Phi_{qi}$ should be expanded in the linearly independent density, temperature, and velocity gradients, i.e.,[6]

$$\Phi_{qi}=-\mathbf{A}_{qi}\cdot\frac{\partial}{\partial\mathbf{r}}\ln(T)-\mathbf{B}_{qi}:\mathbf{S}+n\sum_{q'}(\mathbf{C}^{q'}_{qi}\cdot\mathbf{d}_{q'})-D_{qi}\frac{\partial}{\partial\mathbf{r}}\cdot\mathbf{v}_0\;,\quad(4)$$

where the various terms are defined in Ref. 6. The last term in Eq. (4) is associated with the bulk viscosity which is related to the relaxation time.[2] When the last term in Eq. (4) is substituted into the set of integral equations for $\Phi_{qi}$, the following set of integral equations for $D_{qi}$ is obtained;

$$f^{\circ}_{qi}\frac{c_{int}}{c_v}\left[(1-\tfrac{2}{3}W_q^2)+\frac{k}{c_{int}}(\epsilon_{qi}-\bar{\epsilon}_q)\right]=\sum_{q'} I(D_{qi}) \tag{5}$$

where $I(D_{qi})$ is defined by Eq. (19) in Ref. 6.

## II. THE BULK VISCOSITY

The pressure tensor is defined by

$$\mathbf{p}=\sum_q n_q m_q\langle \mathbf{V}_q\mathbf{V}_q\rangle=\sum_q\sum_i \mathrm{Tr}\int m_q\mathbf{V}_q\mathbf{V}_q f_{qi}\,d\mathbf{v}_q \ ,$$

where the symbol Tr indicates the trace over internal states. To first order in the distribution function, this becomes

$$\mathbf{p}=\sum_q\sum_i \mathrm{Tr}\int(\tfrac{1}{3}\mathbf{U}m_q V_q^2 f^{\circ}_{qi}+m_q\mathbf{V}_q\mathbf{V}_q f^{\circ}_{qi}\Phi_{qi})\,d\mathbf{V}_q$$

where $\mathbf{U}$ is the unit tensor. Upon using the fact that

$$\rho U^{\circ}_{tr}=\sum_q\sum_i \mathrm{Tr}\int \tfrac{1}{2}m_q V_q^2 f^{\circ}_{qi}\,d\mathbf{V}_q=\tfrac{3}{2}p \ ,$$

where $U^{\circ}_{tr}$ is the translational energy/gram and $p=nkT$, the expression for the pressure tensor becomes

$$\mathbf{p}=p\mathbf{U}+\sum_q\sum_i \mathrm{Tr}\,m_q\int \mathbf{V}_q\mathbf{V}_q f^{\circ}_{qi}\Phi_{qi}\,d\mathbf{V}_q \ .$$

Upon using Eq. (4) for $\Phi_{qi}$ and eliminating the terms in $\mathbf{A}_{qi}$ and $\mathbf{C}^{q'}_{qi}$ by symmetry, this becomes

$$\mathbf{p}=p\mathbf{U}+\sum_q\sum_i \mathrm{Tr}\int m_q\mathbf{V}_q\mathbf{V}_q f^{\circ}_{qi}\times\left[-\mathbf{B}_{qi}:\mathbf{S}-D_{qi}\frac{\partial}{\partial\mathbf{r}}\cdot\mathbf{v}_0\right]d\mathbf{V}_q \ .$$

The term involving $\mathbf{B}_{qi}$ is related to the shear viscosity and the term involving $D_{qi}$ is related to the bulk viscosity $\kappa$. The bulk viscosity is the coefficient of $-\mathbf{U}\partial/\partial\mathbf{r}\cdot\mathbf{v}_0$, i.e.,

$$\kappa\mathbf{U}=\sum_q\sum_i \mathrm{Tr}\int m_q\mathbf{V}_q\mathbf{V}_q f^{\circ}_{qi}D_{qi}\,d\mathbf{V}_q \tag{6}$$

In order to find $\kappa$, the function $D_{qi}$ must be expanded in a complete set of functions. It is useful to write

$$D_{qi}=D^1_{qi}+D^2_{qi} \ , \tag{7}$$

where

$$D^1_{qi}=\sum_{n,p,t} d^1_{qnpt}S^{(n)}_{1/2}(W_q^2)R^{(0)}_p(\epsilon_{qi})P^{(0)}_t(m^2) \ , \tag{8}$$

and

$$D^2_{qi}=\sum_{n,p,t} d^2_{qnpt}S^{(n)}_{1/2}(W_q^2)R^{(0)}_p(\epsilon_{qi})P^{(1)}_t(m^2)J^2_{qz} \ , \tag{9}$$

where $\mathbf{J}_{qz}$ is the $z$ component of internal angular momentum operator, $d^1_{qnpt}$ and $d^2_{qnpt}$ are expansion coefficients, and the polynomials $S^{(n)}_{1/2}(W_q^2)$, $R^{(0)}_p(\epsilon_{qi})$, $P^{(0)}_t(m^2)$, and $P^{(1)}_t(m^2)$, and their properties are described in Ref. 6. Equation (8) leads to the result for the bulk viscosity found in the absence of spin polarization and Eq. (9) leads to a spin polarization contribution to the bulk viscosity.

In addition, the auxiliary conditions on $D_{qi}$ are

$$\sum_i \mathrm{Tr}\int f^{\circ}_{qi}D_{qi}\,d\mathbf{V}_q=0 \ , \tag{10}$$

$$\sum_q\sum_i \mathrm{Tr}\int m_q f^{\circ}_{qi}\mathbf{V}_q D_{qi}\,d\mathbf{V}_q=0 \ , \tag{11}$$

$$\sum_q\sum_i \mathrm{Tr}\int f^{\circ}_{qi}D_{qi}(\tfrac{1}{2}m_q V_q^2+E_{qi})\,d\mathbf{V}_q=0 \ , \tag{12}$$

$$\sum_q\sum_i \mathrm{Tr}\int f^{\circ}_{qi}D_{qi}\mathbf{J}_q\,d\mathbf{V}_q=0 \ , \tag{13}$$

and

$$\sum_q\sum_i \mathrm{Tr}\int f^{\circ}_{qi}D_{qi}\mathbf{J}_q\mathbf{V}_q\,d\mathbf{V}_q=0 \ , \tag{14}$$

where $\mathbf{J}_q$ is the internal angular momentum operator.

Upon substituting Eqs. (7), (8), and (9) in Eq. (6) and making use of the orthogonality properties of the expansion coefficients, the result

$$\kappa=kT\sum_q n_q(-d^1_{q100}-\tfrac{1}{3}d^2_{q100}+d^1_{q000}+\tfrac{1}{3}d^2_{q000}) \ ,$$

is obtained, subject to the auxiliary conditions

$$d^1_{q000}+\tfrac{1}{3}d^2_{q000}=0 \ , \tag{15}$$

and

$$\sum_q n_q\left[-\tfrac{3}{2}(d^1_{q100}+\tfrac{1}{3}d^2_{q100})+\frac{c_{q\,int}}{k}(d^1_{q010}+\tfrac{1}{3}d^2_{q010})\right]=0 \ . \tag{16}$$

When auxiliary condition (15) is substituted into the expression for the bulk viscosity, the result

$$\kappa=-kT\sum_q n_q(d^1_{q100}+\tfrac{1}{3}d^2_{q100}) \ , \tag{17}$$

is obtained, subject to auxiliary condition (16).

## III. CALCULATION OF THE EXPANSION COEFFICIENTS

The expansion coefficients in Eq. (17) are obtained through the use of a variational principle.[5,9] In order to calculate the coefficients, a trial function for $D_{qi}$ is necessary. The simplest trial function is obtained by taking

$$n=p=t=0\quad n=1;\ p=t=0\quad p=1;\ n=t=0 \tag{18}$$

in Eqs. (8) and (9), i.e.,

$$D_{qi}=d^1_{q100}T^0_{q100}+d^1_{q010}T^0_{q010}+d^2_{q000}T^1_{q000}+d^2_{q100}T^1_{q100}+d^2_{q010}T^1_{q010} \ , \tag{19}$$

where

$$T^0_{qnpt}=S^{(n)}_{1/2}(W_q^2)R^{(0)}_p(\epsilon_{qi})P^{(0)}_t(m^2) \ , \tag{20}$$

and

$$T^1_{qnpt}=S^{(n)}_{1/2}(W_q^2)R^{(0)}_p(\epsilon_{qi})P^{(1)}_t(m^2)J^2_{qz} \ , \tag{21}$$

with

$$T^1_{q100}=P^{(1)}_0(m^2)J^2_{qz}-\tfrac{1}{3} \ . \tag{22}$$

Auxiliary condition (15) has also been used.

A set of five linear equations for the five unknown expansion coefficients in Eq. (19) is obtained by taking integral moments of each term in trial function (19) with Eq. (5). These equations can be written in the form

$$R_{q\nu}=\sum_{q'}\sum_{\nu'=1}^{5}\frac{n_{q'}}{x_{q'}}\,d_{q'\nu'}\,G_{qq'}^{\nu\nu'},\quad \nu=1,\,2,\,3,\,4,\,5\ , \tag{23}$$

where

$$R_{q1}=-x_q\frac{c_{int}}{c_v}\ ,\quad R_{q2}=-x_q\ ,\quad \frac{c_{qint}}{c_v}\ ,\quad R_{q3}=0$$

$$R_{q4}=\tfrac{1}{3}R_{q1}\ ,\quad R_{q5}=\tfrac{1}{3}R_{q2}\ , \tag{24}$$

and

$$d_{q'1}=d^{1}_{q'100}\ ,\quad d_{q'2}=d^{1}_{q'010}\ ,\quad d_{q'3}=d^{2}_{q'000}$$
$$d_{q'4}=d^{2}_{q'100}\ ,\quad d_{q'5}=d^{2}_{q'010}\ . \tag{25}$$

Also, the $G_{qq'}^{\nu\nu'}$ are evaluated in the Appendix.

The set of equations (23) can be solved for the expansion coefficients. Then Eq. (17) becomes

$$\kappa=-\frac{kT}{c_v}\;\frac{\begin{vmatrix} G^{ab}_{qq'} & \begin{matrix} x_q c_{int}\\ x_q c_{qint}\\ 0\\ x_q c_{int}/3\\ x_q c_{qint}/3\end{matrix}\\ x_{q'}\ 0\ 0\ 0\ 0 & 0\end{vmatrix}+\frac{1}{3}\begin{vmatrix} G^{ab}_{qq'} & \begin{matrix} x_q c_{int}\\ x_q c_{qint}\\ 0\\ x_q c_{int}/3\\ x_q c_{qint}/3\end{matrix}\\ 0\ 0\ 0\ x_{q'}\ 0 & 0\end{vmatrix}}{|G^{ab}_{qq'}|} \tag{26}$$

where

$$G^{ab}_{qq'}=\begin{bmatrix} G^{11}_{qq'} & G^{12}_{qq'} & G^{13}_{qq'} & G^{14}_{qq'} & G^{15}_{qq'}\\ G^{21}_{qq'} & G^{22}_{qq'} & G^{23}_{qq'} & G^{24}_{qq'} & G^{25}_{qq'}\\ G^{31}_{qq'} & G^{32}_{qq'} & G^{33}_{qq'} & G^{34}_{qq'} & G^{35}_{qq'}\\ G^{41}_{qq'} & G^{42}_{qq'} & G^{43}_{qq'} & G^{44}_{qq'} & G^{45}_{qq'}\\ G^{51}_{qq'} & G^{52}_{qq'} & G^{53}_{qq'} & G^{54}_{qq'} & G^{55}_{qq'}\end{bmatrix} \tag{27}$$

Equation (26) is the formal result for the bulk viscosity, including the effect of spin polarization.

## IV. DISCUSSION

In the absence of spin polarization the results given by Eq. (26) and in the Appendix reduce to those in Ref. 2, i.e., the second term in Eq. (26) does not contribute to the bulk viscosity and the only nonzero matrix elements, $G_{qq'}^{\nu\nu'}$, are $G^{11}_{qq'}$, $G^{12}_{qq'}$, $G^{21}_{qq'}$, and $G^{22}_{qq'}$.

The relation between the relaxation time, $\tau$, and the bulk viscosity is[2]

$$\tau=(c_v^2/k\,c_{int}\,p)\kappa \tag{28}$$

in the limit of both easy and difficult interchange of internal and translational energy.

This work is motivated by the desire to obtain numerical results for transport properties, including spin polarization effects, using reasonable simplifying assumptions and realistic intermolecular potentials. The complicated formal results obtained for the spin polarization contribution to transport properties indicates that this is a very difficult task. However, there is reason to believe that this is a tractable problem for relaxation times.

In order to discuss this point, it is necessary to examine those aspects of the problem of evaluating the relaxation time that remain. While Eqs. (26) and (28) give the formal kinetic theory result for the relaxation time, including the contribution from spin polarization, the associated problem of determining scattering cross sections and integrals over scattering cross sections has not been discussed. The complete numerical evaluation of the $G_{qq'}^{\nu\nu'}$ requires explicit expressions for the cross section.

The determination of explicit and computationally useful expressions for scattering cross sections is usually difficult. As an example, formal results for the cross section when rigid diatomic molecules collide involve a great deal of notation because of the relatively large number of angular momenta involved and the need to couple angular momentum states.[10] In particular, these expressions involve a number of summations over angular momenta and the summations present perhaps the greatest difficulty in the numerical calculation of transport properties.

For inelastic collision processes, coupling between states reduces the summations. Most transport properties depend on both elastic and inelastic collisions but relaxation processes depend only on inelastic collisions. Thus the reduced summations over internal states makes the numerical calculation of relaxation times a more tractable problem than the calculation of other transport properties. Indeed Olmsted and Curtiss[11] have obtained an analytical semiclassical result for the rotational relaxation time, in the absence of spin polarization, for a gas of rigid spheres with embedded point dipoles.

Thus the numerical calculation of the spin polarization contribution to the rotational relaxation times appears to be a tractable problem and such a calculation is in progress.

## APPENDIX

Explicit expressions for the $G_{qq'}^{\nu\nu'}$ are obtained by taking integral moments of each term in trial function (19) with Eq. (5). Upon using the first two terms in trial function (19), the result is

$$R_{qnpt}=\sum_i \int T^0_{qnpt}\sum_{q'} I(D_{qi})\,d\mathbf{v}_q \ ,$$

where $n=1;\ p=t=0$ or $p=1;\ n=t=0$ and

$$R_{qnpt}=-n_q\frac{c_{int}}{c_v}\left[\delta(npt;100)+\frac{c_{q\,int}}{c_v}\delta(npt;010)\right]\cdot$$

Upon using the explicit expression for $I(D_{qi})$, this becomes

$$R_{qnpt}=\sum_{q'}\sum_{ijkl}\int\cdots\int T^0_{qnpt}f^\circ_{qi}f^\circ_{q'j}(D_{qi}+D_{q'j}-D'_{qk}-D'_{q'l})\,g\bar{I}^{kl}_{ij}(g,\chi,\phi)(2l_q+1)(2l_{q'}+1)\sin\chi\,d\chi\,d\phi\,d\mathbf{v}_q\,d\mathbf{v}_{1q'}$$

$$=\sum_{q'}n_qn_{q'}\{[T^0_{qnpt};D_{qi}]_{qq'}+[T^0_{qnpt};D_{q'j}]_{qq'}\}\ ,\tag{A1}$$

where

$$[T^0_{qnpt};D_{qi}]_{qq'}=\frac{1}{n_qn_{q'}}\sum_{ijkl}\int\cdots\int T^0_{qnpt}f^\circ_{qi}f^\circ_{q'j}(D_{qi}-D'_{qk})\,g\bar{I}^{kl}_{ij}(g,\chi,\phi)(2l_q+1)(2l_{q'}+1)\sin\chi\,d\chi\,d\phi\,d\mathbf{v}_q\,d\mathbf{v}_{1q'}\ ,\tag{A2}$$

and the degeneracy averaged cross section, $\bar{I}^{kl}_{ij}(g,\chi,\phi)$, is defined by[12]

$$\bar{I}^{kl}_{ij}(g,\chi,\phi)=\frac{1}{(2l_q+1)}\frac{1}{(2l_{q'}+1)}\sum_{z\text{ component states}} I^{kl}_{ij}(g,\chi,\phi)\ .$$

The indices $l_q$ and $l_{q'}$ represent the total angular momentum quantum numbers of molecules $q$ and $q'$, respectively, before collision.

Upon substituting trial function (19) in Eq. (A1), it can be written as

$$R_{qnpt}=\sum_{q'}\sum_{n'p't'}(d^1_{q'n'p't'}\,T^{npt;n'p't'}_{qq'00}+d^2_{q'n'p't'}\,T^{npt;n'p't'}_{qq'01})\ ,\tag{A3}$$

where the possible values of $n', p'$, and $t'$ are

$n'=1;\ p'=t'=0,\quad p'=1;\ n'=t'=0$ ,

in the first term on the right and

$n'=p'=t'=0,\quad n'=1;\ p'=t'=0,\quad p'=1;\ n'=t'=0$ ,

in the second term on the right. Also

$$T^{npt;n'p't'}_{qq'0a}=\sum_{q''}n_qn_{q''}\{\delta_{qq'}[T^0_{qnpt};T^a_{qn'p't'}]_{qq''}+\delta_{q'q''}[T^0_{qnpt};T^a_{q''n'p't'}]_{qq''}\}\ ,\tag{A4}$$

where $a$ is 0 or 1.

Auxiliary condition (15) has already been used. Auxiliary condition (16) can be incorporated into Eq. (A3), i.e.,

$$R_{qnpt}=\sum_{q'}\sum_{n'p't'}(d^1_{q'n'p't'}\,\tilde{T}^{npt;n'p't'}_{qq'00}+d^1_{q'n'p't'}\,\tilde{T}^{npt;n'p't'}_{qq'01})\ ,\tag{A5}$$

where

$$\tilde{T}^{npt;n'p't'}_{qq'00}=T^{npt;n'p't'}_{qq'00}-\left(\frac{\frac{3}{2}n_{q'}\delta(n'p't';100)-n_{q'}\frac{C_{q'\,int}}{k}\delta(n'p't';010)}{\frac{3}{2}n_q\delta(npt;100)-n_q\frac{C_{q\,int}}{k}\delta(npt;010)}\right)T^{npt;npt}_{qq00}\ ,\tag{A6}$$

and

$$\tilde{T}^{npt;n'p't'}_{qq'01}=T^{npt;n'p't'}_{qq'01}-\left(\frac{\frac{1}{2}n_{q'}\delta(n'p't';100)-\frac{1}{3}n_{q'}\frac{C_{q'\,int}}{k}\delta(n'p't';010)}{\frac{3}{2}n_q\delta(npt;100)-n_q\frac{C_{q\,int}}{k}\delta(npt;010)}\right)T^{npt;npt}_{qq00}\ .\tag{A7}$$

The auxiliary condition has been incorporated into the set of linear equations in this particular way so that the results reduce to those of Monchick, Yun, and Mason[2] in the absence of spin polarization.

Upon taking integral moments of the last three terms in trial function (19) with Eq. (5) and using arguments similar to those used to obtain Eq. (A3), the result

$$\tfrac{1}{3}R_{qnpt}=\sum_{q'}\sum_{n'p't'}\left(d^{1}_{q'n'p't'}\,T^{npt;n'p't'}_{qq'10}+d^{2}_{q'n'p't'}\,T^{npt;n'p't'}_{qq'11}\right)\ , \tag{A8}$$

is obtained where the possible values of $n$, $p$, and $t$ are

$$n=p=t=0,\qquad n=1;\ p=t=0,\qquad p=1;\ \ n=t=0\ ,$$

and the possible values of $n'$, $p'$, and $t'$ are

$$n'=1;\ \ p'=t'=0,\qquad p'=1;\ \ n'=t'=0\ ,$$

in the first term of the right and

$$n'=p'=t'=0,\quad n'=1;\quad p'=t'=0,\quad p'=1;\quad n'=t'=0$$

in the second term on the right. Also

$$T^{npt;n'p't'}_{qq'1a}=\sum_{q''}n_q n_{q''}\{\delta_{qq'}[T^{1}_{qnpt};T^{a}_{qn'p't'}]_{qq''}+\delta_{q'q''}[T^{1}_{qnpt};T^{a}_{q''n'p't'}]_{qq''}\}\ , \tag{A9}$$

where $a$ is 0 or 1.

Define

$$\tilde{G}^{npt;n'p't'}_{qq'ab}=\frac{x_q x_{q'}}{g_{qnpt}\,g_{q'n'p't'}}\,\tilde{T}^{npt;n'p't'}_{qq'ab}\ , \tag{A10}$$

and

$$G^{npt;n'p't'}_{qq'ab}=\frac{x_q x_{q'}}{g_{qnpt}\,g_{q'n'p't'}}\,T^{npt;n'p't'}_{qq'ab}\ , \tag{A11}$$

where

$$g_{qnpt}=-n_q[\delta(npt;000)+\delta(npt;100)+\delta(npt;010)]\ . \tag{A12}$$

Upon using these definitions, the set of equations given by Eq. (A5) can be written as

$$R_{qnpt}=\sum_{q'}\sum_{n'p't'}\frac{n_{q'}}{x_{q'}}\left(d^{1}_{q'n'p't'}\,\tilde{G}^{npt;n'p't'}_{qq'00}+d^{2}_{q'n'p't'}\,\tilde{G}^{npt;n'p't'}_{qq'01}\right)\ , \tag{A13}$$

and the set of integral equations given by Eq. (A8) can be written as

$$\tfrac{1}{3}R_{qnpt}=\sum_{q'}\sum_{n'p't'}\frac{n_{q'}}{x_{q'}}\left(d^{1}_{q'n'p't'}\,G^{npt;n'p't'}_{qq'10}+d^{2}_{q'n'p't'}\,G^{npt;n'p't'}_{qq'11}\right)\ . \tag{A14}$$

Upon using Eqs. (24) and (25), Eqs. (A13) and (A14) can be written in the form of Eq. (23) where the expressions for the $G^{\nu\nu'}_{qq'}$ are given below.

It is easily shown that the results in the absence of spin polarization; i.e.,

$$\tilde{G}^{100,100}_{qq'00}=G^{11}_{qq'},\qquad \tilde{G}^{100,010}_{qq'00}=G^{12}_{qq'},\qquad \tilde{G}^{010,100}_{qq'00}=G^{21}_{qq'},\qquad \tilde{G}^{010,010}_{qq'00}=G^{22}_{qq'}\ ,$$

are the same as the results obtained by Monchick, Yun, and Mason.[2] However, when the degeneracy averaged cross section is used, then results should also include the statistical weights $(2l_q+1)(2l_{q'}+1)$.

Now consider the expressions for $\tilde{G}^{npt;n'p't'}_{qq'01}$. Using Eqs. (A4), (A7), (A10), and (A12),

$$\tilde{G}^{100,000}_{qq'01}=G^{13}_{qq'}=\sum_{q''}x_q x_{q''}\{\delta_{qq'}[T^{0}_{q100};T^{1}_{q000}]_{qq''}+\delta_{q'q''}[T^{0}_{q100};T^{1}_{q''000}]_{qq''}\}\ .$$

Upon using Eqs. (20), (22), and (A2), and integrating over the velocity of the center of mass, this becomes

$$G^{13}_{qq'}=4\sum_{q''}\frac{x_q x_{q''}}{Q_q Q_{q''}}\sqrt{\frac{kT}{2\pi\mu}}\,M_{q''}\sum_{ijkl}\int\cdots\int e^{-(\gamma^2+\epsilon_{qi}+\epsilon_{q''j})}\,\Delta\epsilon_{qq''}\left[\delta_{qq'}\left(\frac{m'^2}{k(k+1)}-\frac{m^2}{i(i+1)}\right)+\delta_{q'q''}\left(\frac{m^2_{q''}}{l(l+1)}-\frac{m'^2_{q''}}{j(j+1)}\right)\right]$$
$$\times\gamma^3\tilde{I}^{kl}_{ij}(\gamma,\chi,\phi)(2i+1)(2j+1)\sin\chi\,d\chi\,d\phi\,d\gamma\ , \tag{A15}$$

where

$$\mu=\frac{m_q m_{q''}}{m_q+m_{q''}}\qquad \Delta\epsilon_{qq''}=\epsilon_{qk}+\epsilon_{q''l}-\epsilon_{qi}-\epsilon_{q''k}=\gamma^2-\gamma'^2\ ,$$

and

$$M_q=\frac{m_q}{m_q+m_{q''}}\qquad M_{q''}=\frac{m_{q''}}{m_q+m_{q''}}\qquad \gamma=\sqrt{\frac{\mu}{2kT}}\,g\ .$$

Each of the sums over $i$, $j$, $k$, and $l$ involves a sum over the total angular momentum quantum number and the $z$ component of angular momentum quantum number. However the degeneracy averaged cross section does not depend on the $z$ component of angular momentum quantum numbers. Thus equation (A15) can be written as

$$G^{13}_{qq'} = 4\sum_{q''} \frac{x_q x_{q''}}{Q_q Q_{q''}} \sqrt{\frac{kT}{2\pi\mu}}\, M_{q''} \sum_{ijkl} \int \cdots \int e^{-(\gamma^2+\epsilon_{qi}+\epsilon_{q''j})}\, \Delta\epsilon_{qq''}\, \gamma^3 \bar{I}^{kl}_{ij}(\gamma,\chi,\phi)\,(2i+1)(2j+1)\sin\chi\, d\chi\, d\phi\, d\gamma$$
$$\times \sum_{m,m',m_{q''},m'_{q''}} \{\delta_{qq'}[m'^2 P_0^{(1)}(m'^2) - m^2 P_0^{(1)}(m^2)] + \delta_{q'q''}[m'^2_{q''} P_0^{(1)}(m'^2_{q''}) - m^2_{q''} P_0^{(1)}(m^2_{q''})]\} ,$$

where the indices $i$, $j$, $k$, and $l$ now denote only total orbital angular momentum quantum numbers. Upon using the orthogonality properties of the polynomials, this becomes

$$G^{13}_{qq'} = \frac{8}{3}\sum_{q''} x_q x_{q''} M_{q''} \langle \Delta\epsilon_{qq''}[\delta_{qq'}(2k+1) - \delta_{q'q''}(2l+1)]\rangle_{qq''} , \tag{A16}$$

where

$$\langle F\rangle_{qq''} = \frac{1}{Q_q Q_{q''}} \sqrt{\frac{kT}{2\pi\mu}} \sum_{ijkl} \int \cdots \int e^{-(\gamma^2+\epsilon_{qi}+\epsilon_{q''j})} \gamma^3 \bar{I}^{kl}_{ij}(\gamma,\chi,\phi)(2i+1)(2j+1)\sin\chi\, d\chi\, d\phi\, d\gamma\, F .$$

The other $G^{\nu\nu'}_{qq'}$ are evaluated in a similar manner. The results are

$$G^{14}_{qq'} = \frac{8}{3}\sum_{q''} x_q x_{q''} M_{q''} \langle \Delta\epsilon_{qq''}[\delta_{qq'}(\tfrac{3}{2} - \tfrac{3}{2}M_q - M_{q''}\gamma^2)(2k+1) + \delta_{q'q''}(\tfrac{3}{2} - \tfrac{3}{2}M_{q''} - M_q\gamma'^2)(2l+1)]\rangle_{qq''}$$
$$+ \frac{16}{3}\sum_{q''} x_q x_{q''} M_q M_{q''} \langle (\gamma^2 - \gamma\gamma'\cos\chi)[\delta_{qq'}(2i+1) - \delta_{q'q''}(2j+1)]\rangle_{qq''} - \tfrac{2}{3} x_q x_{q'} \langle \Delta\epsilon^2_{qq'}\rangle_{qq}$$
$$- \frac{4}{3}\sum_{q''\neq q} \frac{x_{q'} x_{q''}}{(m_q + m_{q''})^2}[m^2_{q''}\langle \Delta\epsilon^2_{qq''}\rangle_{qq''} + 4 m_q m_{q''} \Omega^{(1,1)}_{qq''}] . \tag{A17}$$

$$G^{15}_{qq'} = \frac{8}{3}\sum_{q''} x_q x_{q''} M_{q''} \langle \Delta\epsilon_{qq''}[\delta_{qq'}(\epsilon_{qk} - \bar{\epsilon}_q)(2k+1) + \delta_{q'q''}(\epsilon_{q''l} - \bar{\epsilon}_{q''})(2l+1)]\rangle_{qq''} + \frac{4x_q x_{q'} c_{q'int}}{9k}\langle \Delta\epsilon^2_{qq'}\rangle_{qq}$$
$$+ \frac{8 x_{q'} c_{q'int}}{9k} \sum_{q''\neq q} \frac{x_{q''}}{(m_q + m_{q''})^2}\{m^2_{q''}\langle \Delta\epsilon^2_{qq''}\rangle_{qq''} + 4 m_q m_{q''}\Omega^{(1,1)}_{qq''}\} , \tag{A18}$$

$$G^{23}_{qq'} = \frac{8}{3}\sum_{q''} x_q x_{q''} \langle \Delta\epsilon_q\{\delta_{qq'}(2k+1) + \delta_{q'q''}(2l+1)\}\rangle_{qq''} , \tag{A19}$$

$$G^{24}_{qq'} = \frac{8}{3}\sum_{q''} x_q x_{q''} \langle \Delta\epsilon_q[\delta_{qq'}(\tfrac{3}{2} - \tfrac{3}{2}M_q - M_{q''}\gamma'^2)(2k+1) + \delta_{q'q''}(\tfrac{3}{2} - \tfrac{3}{2}M_{q''} - M_q\gamma'^2)(2l+1)]\rangle_{qq''}$$
$$+ \frac{k x_q x_{q'}}{c_{q int}}\langle \Delta\epsilon^2_{qq'}\rangle_{qq} + \frac{2k x_{q'}}{c_{q int}}\sum_{q''\neq q} x_{q''}\langle \Delta\epsilon^2_{qq''}\rangle_{qq''} , \tag{A20}$$

and

$$G^{25}_{qq'} = \frac{8}{3}\sum_{q''} x_q x_{q''} \langle \Delta\epsilon_q[\delta_{qq'}(\epsilon_{qk} - \bar{\epsilon}_q)(2k+1) + \delta_{q'q''}(\epsilon_{q''l} - \bar{\epsilon}_{q''})(2l+1)]\rangle_{qq''} - \frac{2x_q x_{q'} c_{q'int}}{3c_{q int}}\langle \Delta\epsilon^2_{qq'}\rangle_{qq}$$
$$- \frac{4x_{q'} c_{q'int}}{3c_{q int}} \sum_{q''\neq q} x_{q''}\langle \Delta\epsilon^2_{qq''}\rangle_{qq''} , \tag{A21}$$

where $\Delta\epsilon_q = \epsilon_{qk} - \epsilon_{qi}$ and $\Omega^{(1,1)}_{qq''}$ is defined in Ref. 2.

Also

$$G^{31}_{qq'} = \frac{8}{3}\sum_{q''} x_q x_{q''} M_{q''} \langle \Delta\epsilon_{qq''}[\delta_{qq'}(2k+1) + \delta_{q'q''}(2l+1)]\rangle_{qq''} , \tag{A22}$$

$$G^{32}_{qq'} = \frac{8}{3}\sum_{q''} x_q x_{q''} \langle \Delta\epsilon_q[\delta_{qq'}(2k+1) + \delta_{q'q''}(2l+1)]\rangle_{qq''} , \tag{A23}$$

$$G^{33}_{qq'} = \frac{8}{9}\sum_{q''} x_q x_{q''} \langle (2i+1)\{\delta_{qq'}[(2i+1) - (2k+1)] + \delta_{q'q''}[(2j+1) - (2l+1)]\}\rangle_{qq''} , \tag{A24}$$

$$G^{34}_{qq'} = \frac{8}{9}\sum_{q''} x_q x_{q''} \langle [(2i+1) - (2k+1)][\delta_{qq'}(\tfrac{3}{2} - \tfrac{3}{2}M_q - M_{q''}\gamma^2)(2i+1) + \delta_{q'q''}(\tfrac{3}{2} - \tfrac{3}{2}M_{q''} - M_q\gamma^2)(2j+1)]\rangle_{qq''} , \tag{A25}$$

and

$$G^{35}_{qq'} = \frac{8}{9}\sum_{q''} x_q x_{q''} \langle [(2i+1) - (2k+1)][\delta_{qq'}(\epsilon_{qi} - \bar{\epsilon}_q)(2i+1) + \delta_{q'q''}(\epsilon_{q''j} - \bar{\epsilon}_{q''})(2j+1)]\rangle_{qq''} . \tag{A26}$$

In addition

$$G^{41}_{qq'}=\frac{8}{3}\sum_{q''}x_q x_{q''}M_{q''}\langle\Delta\epsilon_{qq''}[\delta_{qq'}(\tfrac{3}{2}-\tfrac{3}{2}M_q-M_{q''}\gamma'^2)(2k+1)+\delta_{q'q''}(\tfrac{3}{2}-\tfrac{3}{2}M_{q''}-M_q\gamma'^2)(2l+1)]\rangle_{qq''}$$
$$+\frac{16}{3}\sum_{q''}x_q x_{q''}M_q M_{q''}\langle(\gamma^2-\gamma\gamma'\cos\chi)[\delta_{qq'}(2i+1)-\delta_{q'q''}(2j+1)]\rangle_{qq''}\ , \tag{A27}$$

$$G^{42}_{qq'}=\frac{8}{3}\sum_{q''}x_q x_{q''}\langle\Delta\epsilon_q[\delta_{qq'}(\tfrac{3}{2}-\tfrac{3}{2}M_q-M_{q''}\gamma'^2)(2k+1)+\delta_{q'q''}(\tfrac{3}{2}-\tfrac{3}{2}M_{q''}-M_q\gamma'^2)(2l+1)]\rangle_{qq''}\ , \tag{A28}$$

$$G^{43}_{qq'}=G^{34}_{qq'}\ , \tag{A29}$$

$$G^{44}_{qq'}=\frac{4}{3}\sum_{q''}x_q x_{q''}\langle\{[(2i+1)-(2k+1)](1-M_q)+\tfrac{2}{3}M_{q''}[\gamma'^2(2k+1)-\gamma^2(2i+1)]\}$$
$$\times[\delta_{qq'}(\tfrac{3}{2}-\tfrac{3}{2}M_q-M_{q''}\gamma^2)(2i+1)+\delta_{q'q''}(\tfrac{3}{2}-\tfrac{3}{2}M_{q''}-M_q\gamma^2)(2j+1)]\rangle_{qq''}$$
$$-\frac{4}{3}\sum_{q''}x_q x_{q''}M_q\langle[(2i+1)-(2k+1)][\delta_{qq'}M_q(2k+1)+\delta_{q'q''}M_{q''}(2l+1)]\rangle_{qq''}$$
$$+\frac{16}{9}\sum_{q''}x_q x_{q''}M_q M_{q''}\langle(2i+1)\{\delta_{qq'}[\gamma^2(2i+1)-(2k+1)\gamma\gamma'\cos\chi]+\delta_{q'q''}[(2l+1)\gamma\gamma'\cos\chi-\gamma^2(2j+1)]\}\rangle_{qq''}\ , \tag{A30}$$

and

$$G^{45}_{qq'}=\frac{8}{9}\sum_{q''}x_q x_{q''}\langle(\tfrac{3}{2}-\tfrac{3}{2}M_q-M_{q''}\gamma^2)(2i+1)\{\delta_{qq'}[(\epsilon_{qi}-\bar{\epsilon}_q)(2i+1)-(\epsilon_{qk}-\bar{\epsilon}_q)(2k+1)]$$
$$+\delta_{q'q''}[(\epsilon_{q''j}-\bar{\epsilon}_{q''})(2j+1)-(\epsilon_{q''l}-\bar{\epsilon}_{q''})(2l+1)]\}\rangle_{qq''}\ . \tag{A31}$$

Finally

$$G^{51}_{qq'}=\frac{8}{3}\sum_{q''}x_q x_{q''}M_{q''}\langle\Delta\epsilon_{qq''}[\delta_{qq'}(\epsilon_{qk}-\bar{\epsilon}_q)(2k+1)+\delta_{q'q''}(\epsilon_{q''l}-\bar{\epsilon}_{q''})(2l+1)]\rangle_{qq''}\ , \tag{A32}$$

$$G^{52}_{qq'}=\frac{8}{3}\sum_{q''}x_q x_{q''}\langle\Delta\epsilon_q[\delta_{qq'}(\epsilon_{qk}-\bar{\epsilon}_q)(2k+1)+\delta_{q'q''}(\epsilon_{q''l}-\bar{\epsilon}_{q''})(2l+1)]\rangle_{qq'}\ , \tag{A33}$$

$$G^{53}_{qq'}=G^{35}_{qq'}\ , \tag{A34}$$

$$G^{54}_{qq'}=G^{45}_{qq'}\ , \tag{A35}$$

and

$$G^{55}_{qq'}=\frac{8}{9}\sum_{q''}x_q x_{q''}\langle(\epsilon_{qi}-\bar{\epsilon}_q)(2i+1)\{\delta_{qq'}[(\epsilon_{qi}-\bar{\epsilon}_q)(2i+1)-(\epsilon_{qk}-\bar{\epsilon}_q)(2k+1)]$$
$$+\delta_{q'q''}[(\epsilon_{q''j}-\bar{\epsilon}_{q''})(2j+1)-(\epsilon_{q''l}-\bar{\epsilon}_{q''})(2l+1)]\}\rangle_{qq''}\ . \tag{A36}$$


[1]C. S. Wang Chang, G. E. Uhlenbeck, and J. de Boer, "The Heat Conductivity and Viscosity of Polyatomic Gases" in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (Wiley, New York, 1964).

[2]L. Monchick, K. S. Yun, and E. A. Mason, J. Chem. Phys. **39**, 654 (1963).

[3]Y. Kagan and A. M. Afanas'ev, Sov. Phys. JETP **14**, 1096 (1962).

[4]S. I. Sandler and J. S. Dahler, J. Chem. Phys. **47**, 2621 (1967).

[5]F. R. McCourt and R. F. Snider, J. Chem. Phys. **41**, 3185 (1964).

[6]L. Biolsi and E. A. Mason, J. Chem. Phys. **63**, 10 (1975). There is an error in the notation in Eqs. (4), (5), (6), (7), (8), (15), (25), (26), (27), and (28). Each of these equations involves the trace over internal states; e.g., Eq. (8) should be

$$\mathbf{J}=\sum_q\sum_i \mathrm{Tr}\int f^{\circ}_{qi}\mathbf{J}_q\,d\mathbf{v}_q\ .$$

[7]L. Biolsi and E. A. Mason, Proc. 14th Int. Conf. Thermal Conductivity (in press).

[8]S. I. Sandler and E. A. Mason, J. Chem. Phys. **47**, 4653 (1967).

[9]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[10]D. Russell and C. F. Curtiss, J. Chem. Phys. **60**, 1313 (1974). This paper refers to earlier papers in the series.

[11]R. D. Olmsted and C. F. Curtiss, J. Chem. Phys. **55**, 3276 (1971).

[12]G. Gioumousis and C. F. Curtiss, J. Math. Phys. **2**, 96 (1961).