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Density Effects in Internal-Energy Transport in Polyatomic Gases[1]

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The revised Enskog theory is used in a heuristic way to modify the Wang Chang–Uhlenbeck quantum kinetic equation for polyatomic gases close to thermodynamic equilibrium. The density effects predicted for the total and internal thermal conductivities are in qualitative agreement with recent molecular dynamic calculations, suggesting that inelastic effects should be included in dense fluid transport theory.

KEY WORDS: density; internal energy; polyatomic gases; revised Enskog theory; rotational relaxation; thermal conductivity; transport properties; Wang Chang–Uhlenbeck equation.

1. INTRODUCTION

The Wang Chang–Uhlenbeck quantum kinetic equation (WCUE) [1, 2] can be shown to be the degeneracy averaged form of the Waldman–Snider quantum kinetic equation (WSE) [3, 4], the proper quantum extension of the classical Boltzman equation [5, 6]. WCUE had its initial success when Mason and Monchick [7] used it to describe the thermal conductivity of polyatomic gases with internal degrees of freedom. WSE, which is more general, can describe processes which WCUE cannot: Senftleben–Beenakker effects [8] and rotovibrational line shapes [9, 10] The drawback of both WSE and WCUE is that they are limited to low and moderate molecular densities where only isolated two molecule collisions are nonnegligible. Although an analogue to the classical modified Enskog theory has appeared [11], it has not as yet been applied to the description of gas transport properties at high pressures. In particular, no high-density

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analogue of the Mason–Monchick thermal conductivity [7] approximation exists.

In lieu of a true WCU or WSE theory of thermal conductivity of polyatomic gases, there are two *ad hoc* marriages [6, 12] of low-density Eucken expressions and standard [6] or revised Enskog [12, 13] theories of classical rigid spheres and one set of molecular-dynamics calculations [14]. Each study predicts a different density dependence of the internal state thermal conductivity, λ_{int}. The present study suggests the reason for this disparity and outlines a heuristic theory of high-density thermal conductivity.

In the Castillo–Orozco paper [12], the density dependence of the revised Enskog theory (RET) [13] of classical smooth rigid spheres (CSRS) is added to the modified Eucken theory (cf. Ref. 6, Sect. 7.6b) of the thermal conductivity of polyatomic gases. That is, λ_{int} is taken to be proportional to $nm\mathscr{D}/\chi$, the number density, n, times the mass, m, times the self-diffusion coefficient, $\mathscr{D}$, divided by the relative molecular distribution, χ, evaluated at the molecular distance of closest approach. As reported in the next section, this is consistent with RET and the assumption of negligible inelasticity: λ_{int} is found to make a contribution to λ_{tot}, the total thermal conductivity, which is significant at low, but negligible at high, densities. The agreement with empirical correlations is not too bad. A similar assumption utilizing SET, the standard Enskog theory, [5] is made in Section 9.3e-ii of *The Molecular Theory of Gases and Liquids* [6] (MTGL). This leads to a λ_{int} varying like $nm\mathscr{D}$, i.e., independently of pressure; if this were applied to the same data, it would worsen the agreement with theory markedly. The SET- and the RET-based theories both neglect rotational relaxation. In contrast, the molecular-dynamics results conducted with a model diatomic fluid [14] predict that λ_{int} increases significantly with density and that the ratio, $\lambda_{\text{int}}/\lambda_{\text{tot}}$, decreases initially and then seems to reach a finite asymptote. It is also difficult to reconcile the Castillo–Orozco or the MTGL result with the kinetic theories of classical rough spheres at high densities, which also predict a large dependence on internal state, in this case, spin [15, 16].

In the following, the Wang Chang–Uhlenbeck equation will be modified in an *ad hoc* way to incorporate density effects in the same way that the revised Enskog Theory incorporates them in the classical smooth rigid sphere Boltzmann equation. Solved in the usual manner, the retention of rotational relaxation terms leads to a translational thermal conductivity, λ_{tr}, slightly smaller than the Castillo–Orozco result and to λ_{int} increasing at very high densities at least as quickly as λ_{tr} does. This is qualitatively consistent with the results obtained by Murad et al. [14]. As an added benefit, a more than compensating increase in inelastic terms in λ_{tr} would tend to improve Castillo and Orozco's correlations of the experimental data with RET [12] or theories which start with RET [17]. In the next section the derivation of the thermal conductivity is presented in some detail as a demonstration of how naturally complex density effects can appear in the internal-energy contribution in a kinetic theory of sufficient generality and as a tribute to the memory of Professor Mason, one of whose lasting interests was the theory of thermal conductivity in polyatomic gases.

2. RET–WCU THEORY

The object is to derive not a rigorous formula, but a simple, heuristic, extension of the theory for the thermal conductivity at moderate densities. This extension simply multiplies the degeneracy averaged state-to-state differential scattering cross section, $I_{ij,\,kl}(\hat{\mathbf{k}})$, in the WCUE collision term by the RET function χ [13] and identifies the contact collision-transfer terms with those evaluated by López de Haro et al. [18] for mixtures of smooth rigid spheres. The species indices are then identified as the indices of the internal states, which then, at least for the contact collision transfer terms, are required to be in thermodynamic equilibrium.

Thus the state-to-state differential scattering cross section is replaced as follows:

$$I_{ij,\,kl}(\hat{\mathbf{k}}) \rightarrow I^{\pm}_{ij,\,kl}(\hat{\mathbf{k}}) \equiv I_{ij,\,kl}(\hat{\mathbf{k}})\,\chi_{ij}(\mathbf{r}, \mathbf{r} \pm \sigma_{ij}\hat{\mathbf{k}} \mid \{n_i\}) = I_{ij,\,kl}(\hat{\mathbf{k}})\,\chi^{\pm}_{ij} \tag{1}$$

Here i and j are the initial internal states (degeneracy averaged) of the colliding molecules, k and l are the final values, and χ, the local radial distribution function for a system with nonuniform density evaluated at the distance of closest approach, σ, is an increasing function of the local macroscopic density, $\rho(\mathbf{r})$, evaluated at a given position coordinate, $\mathbf{r}$. The implicit dependence of χ on the local number densities, $\{n_i\}$, is stated to be necessary for the linearized theory to satisfy the Onsager relations [13]. In addition, the local molecular distribution functions must also be evaluated at $\mathbf{r} \pm \sigma\hat{\mathbf{k}}$. The revised Enskog theory/Wang Chang–Uhlenbeck (RET–WCU) equation then becomes

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\frac{\partial}{\partial \mathbf{r}}\right) f_i(\mathbf{r}, \mathbf{v}, t) = \sum_{jkl} \int d\mathbf{v}_1\, d\hat{\mathbf{k}}[\, g' I^{+}_{kl,\,ij}(\hat{\mathbf{k}})\, f_k(\mathbf{r} + \sigma_{kl}\hat{\mathbf{k}}, \mathbf{v}', t)\, f_l(\mathbf{r}, \mathbf{v}'_1, t)$$

$$- g I^{-}_{ij,\,kl}(\hat{\mathbf{k}})\, f_i(\mathbf{r}, \mathbf{v}, t)\, f_j(\mathbf{r} - \sigma_{ij}\hat{\mathbf{k}}, \mathbf{v}_1, t)] \tag{2}$$

Here $\mathbf{v}$ and $\mathbf{v}'$ are the initial and final velocities of the test particle, $\mathbf{v}_1$ and $\mathbf{v}'_1$ are the initial and final velocities of the colliding particle, and $\mathbf{g}$ and $\mathbf{g}'$ are the initial and final relative velocities.

As first shown by Enskog [19, 5], a Chapman–Enskog solution of the Enskog equation can be carried out if the collision term is expanded in powers of σ and the first-order perturbation terms, which can be interpreted as contact collisional transfer terms, are combined with the zeroth-order drift terms. In Eq. (2), the indices i, j, k, l are regarded as species indices and the manifold of internal states as a mixture of distinguishable particles [20] later allowed to exchange identities. This is just a generalization of MTGL's derivation of the modified Eucken approximation [6]. In the limit $\chi \sim 1$, Eq. (2) may be regarded as the degeneracy average of a quantum kinetic equation for reacting molecules [21]. If, for the contact collision transfer processes, it is assumed that changes of internal state are relatively rare, i.e., $I_{ij,kl} \equiv I_{ij,ij}\,\delta_{ik}\,\delta_{kl}$, the contact collision transfer terms can be identified unambiguously as those evaluated by López de Haro et al. [18] for mixtures of unreactive molecules. In this form, the formulae of the linearized RET kinetic equation for mixtures [18, 22] may be carried over unchanged to obtain the linearized RET–WCU equation. With the definitions

$$\begin{aligned} f_i^0(\mathbf{r}, \mathbf{v}, t) &= n_i(m/2\pi kT)^{3/2}\exp(-W^2) \\ &= nx_i(m/2\pi kT)^{3/2}\exp(-W^2) \end{aligned} \tag{3}$$

$$\mathbf{g} = \mathbf{v} - \mathbf{v}_1 \tag{4}$$

$$\mathbf{g}' = \mathbf{v}' - \mathbf{v}'_1 \tag{5}$$

$$\mathbf{W} = (m/2kT)^{1/2}(\mathbf{v} - \mathbf{v}_0) \tag{6}$$

the integral equation for φ, the perturbation to the distribution function in the Chapman–Enskog approximation is, in the absence of shear flow,

$$\begin{aligned} (\Re\varphi)_i &= -\sum_{jkl}\int d\mathbf{v}_1\, d\hat{\mathbf{k}}\, g\chi_c I_{ij,kl}(\hat{\mathbf{k}})\, f_j^0(\mathbf{r}, \mathbf{v}_1, t) \\ &\quad\times[\varphi_i(\mathbf{v}) + \varphi_j(\mathbf{v}_1) - (\varphi_k(\mathbf{v}') + \varphi_l(\mathbf{v}'_1))] \\ &= n\mathbf{d}_i\cdot(\mathbf{v} - \mathbf{v}_0) + n_iK_i(W^2 - 5/2)(\mathbf{v} - \mathbf{v}_0)\cdot\nabla\ln\mathbf{T} \\ &\equiv \mathfrak{D}_i\cdot(\mathbf{v} - \mathbf{v}_0) \end{aligned} \tag{7}$$

$$n = \sum_i\int d\mathbf{v}\, f_i(\mathbf{r}, \mathbf{v}, t) = \sum_i n_i = n\sum_i x_i$$

$$\mathbf{v}_0 = \sum_i\int d\mathbf{v}\, \mathbf{v}f_i(\mathbf{r}, \mathbf{v}, t)$$

$$T=\frac{2}{3}k^{-1}\sum_{i}\int d\mathbf{v}\,\frac{m}{2}(\mathbf{v}-\mathbf{v}_0)^2 f_i(\mathbf{r},\mathbf{v},t) \tag{8}$$

$$\begin{aligned}\mathbf{d}_i=&\frac{x_i}{kT}\sum_{k=1}^{N}\left(\frac{\partial\mu_i}{\partial n_k}\right)\nabla n_k-\frac{x_i}{nkT}\left[\nabla p+\sum_{k=1}^{\infty}n_k(\mathbf{F}_i-\mathbf{F}_k)\right]\\ &+x_i\tilde{K}_i\nabla\ln T\end{aligned} \tag{9}$$

$$K_i=1+\frac{3}{5}\sum_{j=1}^{\infty}n_jB_{ij}\bar{\chi}_{ijc}$$

$$\tilde{K}_i=1+\sum_{j=1}^{\infty}n_jB_{ij}\bar{\chi}_{ijc}$$

$$p=nkT\left(1+n\sum_{j,k=1}^{\infty}x_jx_kB_{jk}\bar{\chi}_{jkc}\right) \tag{10}$$

Here B_{ij}, properly the rigid-sphere second virial coefficient divided by Avogadro's number, is understood to be the real molecule equivalent, where the states i and j are to be treated as distinguishable molecules. We now introduce the first of four simplifications: (i) the requirement that the distribution of internal states on the rhs be close to equilibrium,

$$\begin{aligned}x_i&=Q^{-1}\exp(-\varepsilon_i)\\ \varepsilon_i&=E_i^{\text{int}}/kT\\ Q&=\sum_i\exp(-\varepsilon_i)\end{aligned} \tag{11}$$

This has the effect of reducing the range of distributions described by the density matrix or the necessity for source and/or sink terms in Eq. (9). The chemical potential is generally assumed to have the form [23]

$$\mu_i/kT=\ln n_i+\text{const}+2\sum_j n_jB_{ij}\bar{\chi}_{ij} \tag{12}$$

We now introduce two more simplifications: (ii) the constant in Eq. (12) has the form $-\ln(n\exp(-\varepsilon_i/kT))$; and (iii) $B_{ij}\equiv B$, $\bar{\chi}\equiv\bar{\chi}$, $\forall i, j$. This leads to

$$\mu_i/kT=\ln n_i-\ln(n\exp(-\varepsilon_i/kT))+2nB\bar{\chi} \tag{13}$$

which is now consistent with Eq. (11) and thermodynamic equilibrium, and to

$$\begin{aligned}K_i&=K+1+\tfrac{3}{5}nB\bar{\chi}_c\\ \tilde{K}_i&=\tilde{K}=1+nB\bar{\chi}_c\\ p&=nkT(1+nB\bar{\chi}_c)\end{aligned} \tag{14}$$

Equation (3), (13), (14), the Gibbs–Duhem relation, and the zero external field lead to a simplified drift term, $\mathfrak{D}_i$, composed of a set of two driving terms analogous to chemical potentials:

$$\begin{aligned}
\mathfrak{D}_i &= n_i(\mathbf{d}_i^{\mathrm{T}} + \mathbf{d}_i^{\mathrm{I}}) \cdot (\mathbf{v} - \mathbf{v}_0) \\
\mathbf{d}_i^{\mathrm{T}} &= K(W^2 - 5/2)\, \nabla \ln T = -K\mathcal{S}^1_{3/2}\mathcal{P}_i^0\, \nabla \ln T \qquad (15) \\
\mathbf{d}_i^{\mathrm{I}} &= (kT)^{-1}\, (\varepsilon_i - \bar{\varepsilon})\, \nabla \ln T = \mathcal{S}^0_{3/2}\mathcal{P}_i^1\, \nabla \ln T
\end{aligned}$$

representing, in order, driving terms for the diffusion of kinetic energy and internal energy. $\{\mathcal{S}^n_m(W^2)\}_{n,m}$ are the well-known Sonine polynomials ubiquitous in transport-property theory and $\mathcal{P}_i^r$ are the internal-state orthogonalized polynomials common to many transport property theories of polyatomic molecules [1, 2, 7]. The first two internal-state polynomials are $\mathcal{P}_i^0 = 1$ and $\mathcal{P}_i^1 = (kT)^{-1}\, (\varepsilon_i - \bar{\varepsilon})$. Assumption (3) has enabled us to set

$$\chi^{-1}(\mathfrak{R}\varphi)_i = (\mathfrak{R}^0\varphi)_i = \chi^{-1}\mathfrak{D}_i \qquad (16)$$

where $\mathfrak{R}^0$ is the low-density collision operator. The collision integrals appearing on the lhs will now be the usual ones appearing in moderate-density WCU theory [1, 2, 7], but the rhs driving terms for translational heat flux and for internal-energy flux will now have the new multipliers, $K\chi^{-1}$ and χ^{-1}. The base vectors $\mathcal{S}^n_{3/2}\mathcal{P}_i^m(\mathbf{v} - \mathbf{v}_0)$ span the kinetic variable space relevant to thermal energy flux. With Eq. (15) we see that in the absence of shear flow, the right-hand side of Eq. (7) is composed of just two of them. This suggests the representation

$$\varphi = (c^{\mathrm{T}}\mathcal{S}^1_{3/2}\mathcal{P}_i^0 + c^{\mathrm{I}}\mathcal{S}^0_{3/2}\mathcal{P}_i^1 + \Delta\tilde{\varphi})(\mathbf{v} - \mathbf{v}_0) \cdot \nabla \ln T \qquad (17)$$

The final simplification may now be made. (4) $\Delta\tilde{\varphi}$ is usually small and will be neglected. This reduces the problem of inverting $\mathfrak{R}$ to the inversion of a two-dimensional matrix but it also has eliminated all thermal-diffusion fluxes of the internal states. Since the coupling terms, $\mathfrak{R}_{\mathrm{TI}}$ and $\mathfrak{R}_{\mathrm{IT}}$, do not vanish if rotational relaxation does not vanish, both c^{T} and c^{I}, and thus both λ_{tr} and λ_{int}, will have mixtures of terms proportional to $K\chi^{-1}$ and χ^{-1}. If, as in the moderate-density WCU procedure [1, 2, 6, 7], we make the usual replacements of $\Omega^{(1,1)}$, $\Omega^{(2,2)}$ and the cross terms by the moderate density expressions relating them to the self-diffusion coefficient, $\mathcal{D}$, the shear viscosity, η, and the rotational relaxation time, τ, the RET extension of the Mason–Monchick approximation to the thermal conductivity becomes

$$\lambda_{\text{tr}} = \lambda_{\text{tr}}^{0} \chi^{-1} K \left(1 - \frac{5c_{\text{int}}}{6k} \left(\frac{\eta}{nkT\tau} \right) \left(1 - \frac{2}{5} \frac{nm\mathscr{D}}{\eta} K^{-1} \right) \right) \tag{18}$$

$$\lambda_{\text{int}} = \lambda_{\text{int}}^{0} \chi^{-1} \left(1 + \frac{5}{4} \left(\frac{\eta}{nkT\tau} \right) \left(K - \frac{2}{5} \frac{nm\mathscr{D}}{\eta} \right) \right) \tag{19}$$

$$\lambda_{\text{tr}}^{0} = \frac{15}{4} \frac{k\eta}{m} \tag{20}$$

$$\lambda_{\text{int}}^{0} = \frac{c_{\text{int}} nm\mathscr{D}}{m} \tag{21}$$

where c_{int} is the internal state heat caspacity.

3. DISCUSSION

From Eqs. (18) and (19) it is seen that what was assumed [12, 17] to be the main term of λ_{int} becomes vanishingly small with increasing density and that an initially minor correction term eventually increases as rapidly as λ_{tr}, i.e., that $\lambda_{\text{int}}/\lambda_{\text{tr}} \to \text{const} \ll 1$, in such a way that at sufficiently high n, $\lambda_{\text{int}} \gg \lambda_{\text{int}}^{0}$. This general behavior is qualitatively consistent with the molecular-dynamics results of Murad et al. [14], i.e., at least one component of the internal thermal conductivity does not vanish at high densities. Also, since λ_{tot} is less than λ_{tot} (Castillo and Orozco), a slight improvement on their correlations might be possible. At extremely high densities, where rotations become librations, the theory breaks down.

The final simple formula for the thermal conductivity is based on a two-term expansion of the density matrix. The solution requires the inversion of a two-dimensional matrix equation, $\mathscr{R}\mathbf{c} = \mathscr{D}$, where $\mathscr{D}_{\text{T}}$ varies as $K\chi^{-1}$ and $\mathscr{D}_{\text{I}}$ as χ^{-1}. The $K\chi^{-1}$ dependence of λ_{int} is a direct result of the possibility of rotational relaxation which couples both modes. This particular form of $\mathscr{D}$, in which only two of the basis vectors of the space appear, results from the assumption of thermodynamic equilibrium of internal states in the zeroth approximation. Since $\mathscr{D}$ is not changed by including higher-order terms in φ, the general form of Eqs. (18) and (19) will remain unchanged, even though individual terms will become more complex functions of the collision integrals.

The weak point of this heuristic theory is the adoption of Eq. (1) and the assumption that $I_{ij,kl} \equiv I_{ij,ij} \delta_{ik} \delta_{kl}$ for the contact collision transfer terms. Although for models which can be evaluated exactly, such as rough spheres [15, 16], collision transfer terms of internal state flux and angular momentum flux can be evaluated and turn out to be significant, the moderately successful correlation of Castillo and Orozco [12] and the molecular-dynamics study of Murad *et al.* [14] suggest that the heuristic theory outlined here describes many if not most systems of interest and that rough-sphere models may overestimate rotational energy interchange.

From an engineering point of view, the result is mainly of academic interest. The source of a small discrepancy may have found its explanation, an explanation which suggests that more rigorous theories will not result in further surprises. Fundamentally, it may have other uses. One difficulty in comparing *ab initio* calculations with experiment is that the thermal conductivity is more complex than the shear viscosity: Eq. (18), for instance, is a function of momentum transfer cross sections, $\mathcal{S}$, momentum-flux transfer cross sections, η, and inelastic collisions, τ. The possibility of simultaneous measurements of λ, λ_{tr} (by thermal transpiration or thermal diffusion of micron-size particles), and τ as functions of density may provide alternate ways of checking the internal consisteny of *ab initio* calculations. Another use is that it demonstrates mechanisms that should be included in calculations [12, 17] using RET as a starting point.

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