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INVESTIGATION OF QUANTUM AND CLASSICAL MODELS FOR MOLECULAR RELAXATION USING THE DIRECT SIMULATION MONTE CARLO (DSMC) METHOD

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Abstract

It is widely known that losses due to viscous, thermal and molecular relaxation play an important role in sound propagation. Traditionally, acoustics is concerned with the treatment of the fluid as a (linear) continuum using macroscopic quantities such as velocity and pressure as dependent variables. However, the continuum model has its limitations and the model breaks down for Knudsen numbers (Kn) greater than roughly 0.05, where Kn is defined as the ratio of mean free path to wavelength. Particle or Boltzmann equation methods are necessary for, but not limited to, problems with $Kn > 0.05$. In our studies we have used a particle method, Bird's direct simulation Monte Carlo (DSMC) method, for the direct physical modeling of particle motions and intermolecular collisions in several acoustics problems. Using DSMC to study acoustics allows us to explore real gas effects for all values of Kn with a molecular model that continuum methods cannot offer. DSMC allows us to explore acoustics at varying temperatures, molecular composition, Knudsen numbers, and amplitude. In our current DSMC calculations for gas mixtures we have explored different methods to simulate the internal degrees of freedom in molecules and the exchange of translational, rotational and vibrational energies in collisions of molecules. One of these is the fully classical rigid-rotor/harmonic-oscillator model for rotation and vibration developed by Borgnakke and Larson. A second takes into account the discrete

quantum energy levels for vibration with rotation treated classically. This method gives a more realistic representation of the internal structure of diatomic and polyatomic molecules. A third method considers individual quantum vibrational-rotational levels. In our studies we have investigated the application of these methods in the direct simulation - at the molecular level - of the propagation of sound and its attenuation along with their dependence on temperature for several gas mixtures.

1. INTRODUCTION

There is a hierarchy of mathematical models available to solve fluid dynamics problems. These models have varying degrees of approximation but can be categorized into two groups: continuum methods and particle methods. Continuum methods, which are popular for acoustic problems, model the fluid as a continuous medium. This model describes the state of the fluid with macroscopic level using quantities such as density, velocity, and temperature. The continuum approximation is valid when the characteristic length of the problem is much larger than the molecular spacing between fluid particles. This assumption is satisfied for many engineering problems, and thus fluid evolution can be described using continuum equations such as the Navier-Stokes or Euler equations.

However, the continuum model has its limitations. The macroscopic model assumes deviations from thermal equilibrium are small, and it is the failure of the closure of the Navier-Stokes equations that limit the applications of this approach. The Knudsen number (Kn) which is defined to be the mean free path divided by a characteristic length scale is a measure of the nonequilibrium or viscous effects of the gas. The Knudsen number is also used to distinguish the regimes where different governing equations of fluid dynamics are applicable. The Navier-Stokes equations are valid for $Kn < 0.05$, and the Navier-Stokes equations reduce to the Euler equations as Kn approaches 0. The Boltzmann equation is the mathematical model for particle methods and is valid for all Kn , although most efficient for high Kn . Therefore, particle methods are necessary for, but not limited to, problems where the Knudsen number is greater than 0.05.

Particle methods are based on molecular models that realize the particle nature of the gas and describe the state of the gas at the microscopic level. Despite the fact that the Boltzmann equation was derived using a microscopic approach, it can be shown that the Boltzmann equation will reduce to the continuum conservation equations (e.g Navier-Stokes) for low Kn .

Direct simulation Monte Carlo is a stochastic, particle-based method developed by Bird that is capable of simulating real gas effects for all values of Kn with a molecular model that traditional continuum models cannot offer [1]. The Knudsen number is large for sound propagation in very dilute gases or at high frequencies requiring a particle-method solution. Past results in DSMC that sound absorption depends heavily on Kn for acoustic wave propagation in monatomic gases [2]. Successful application of DSMC to nonlinear acoustic waves has already been shown for monatomic and diatomic gases [3]. We continue to investigate this area with the study of absorption with a more realistic emphasis on the models used for internal energy exchange found in inelastic collisions. Both discrete and continuous models for energy exchange are examined in gaseous Nitrogen at a variety of temperatures and Knudsen numbers to gain a broader understanding of the effects of exchange rates for acoustics applications.

The remainder of the paper is outlined. Section 2 will describe the DSMC method, includ-

ing the initialization of equilibrium systems and details on the internal energy methods used for molecular exchange and relaxation. Section 3 will outline the current theories on the absorption of sound including molecular relaxation phenomenon. Section 4 will outline the initialization and execution of each simulation with specifics on the parallel code and simulation performance. Section 5 will display the results of the DSMC simulations for classical and discrete models for a range of temperatures and Knudsen numbers. Results are compared to classical theory and Navier-Stokes equations and are discussed at length.

2. DIRECT SIMULATION MONTE CARLO

Direct simulation Monte Carlo is a stochastic method used to computationally model gas flows with thousands or millions of representative molecules through the direct physical modeling of particle motions and intermolecular collisions. DSMC is based on the kinetic theory of gases with the movement of particles being determined by their velocities and treated deterministically. On the other hand, collisions are determined statistically (independent of their position in a cell) but are required to conserve mass, momentum, and energy. In DSMC the particle positions and velocities are initialized randomly and the boundary conditions are applied to exhibit the appropriate behavior of the system being modeled and ultimately determine the final solution.

The DSMC program used contains several types of energy models used to treat molecules in gas mixtures with internal energy. Internal energy is divided into rotational and vibrational modes and has been programmed to simulate classical or quantum behavior or a combination of both. The classical model for rotation and vibration was first developed by Borgnakke and Larson [7] and uses a phenomenological approach to handle inelastic collisions between molecules with internal degrees of freedom. Our continuous model based on work by Bird [1] obeys detailed balancing and selects the post-collision internal energies by sampling from known equilibrium distributions associated with a notional temperature based on the collision energy. The rate at which the collisions are inelastic and result in an exchange of energy is a function of both temperature and the molecular species contained within the system.

A second fundamental model used in this research for handling internal energy exchange accounts for the quantum nature of the internal energy of the molecules. This method uses discrete, quantized energy levels to represent the vibrational state of the molecules and is a more realistic representation of the internal structure of diatomic and polyatomic molecules. The model is based primarily on the methods developed by Anderson [4] and Boyd [5] and uses the characteristic temperatures and collision energies to determine the populations of energy levels for a given molecular species.

Simulations of nitrogen with a fully classical rotation-vibration model and a quasi classical rotation-vibration model are given to test the molecular relaxation as a function of the number of collisions per molecule in Figures 1 and 2, respectively. Both simulations were completed under the same conditions in a single cell with a length of 1/2 the mean-free-path, an initial freestream (translational) temperature of 4000 K, and on average 1 out of every 5 collisions were treated as inelastic. Relaxation is the mechanism at which the system exchanges energy between translational and internal modes in order to reach a state of thermal equilibrium. Both cases as compared to simple theoretical treatments (model rates) derived by Bird [1] to determine the validity of the models. Figure 1 shows excellent agreement between the

exponential model and the classical rate of exchange. Figure 2 shows the coupled classical rotation/quantum vibration model and its deviation from an idealized exponential rate. Figure 2 shows a more realistic rate of exchange based on the quantum nature of a populated level and requires more collision per molecule in order to reach equilibrium.

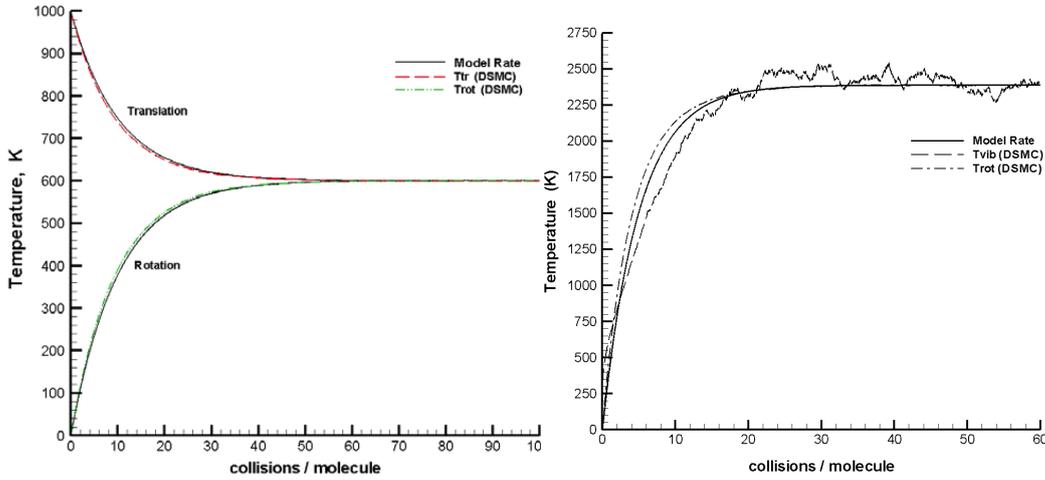


Figure 1. DSMC simulation of N_2 molecules undergoing fully classical relaxation at 4000 K. Figure 2. DSMC simulation of N_2 molecules undergoing a coupled discrete vibration / classical rotation relaxation at 4000 K.

3. THEORY

The physical properties of the absorption of sound include classical losses associated with the transfer of acoustic energy into heat and relaxation losses associated with the redistribution of internal energy of molecules. The relaxation losses can be broken down into those associated with the relaxation of the molecule's rotational energy and the losses associated with the relaxation of the molecule's vibrational energy. The total absorption coefficient α in Np/m is usually written [12] as

$$\alpha = \alpha_{cr} + \alpha_{vib}, \quad (1)$$

where α_{cr} is the combined attenuation due to classical (translational) and rotational relaxation losses and α_{vib} is the attenuation due to vibrational relaxation losses.

Greenspan [10] presents theoretical expressions based on the Navier-Stokes equations for the combined absorption due to classical and rotational relaxation. Greenspan writes the absorption due to translational and rotational relaxation α_{cr} as

$$\alpha_{cr} = \frac{\alpha_{cl}\beta_{rot}}{\beta_0} + \frac{\alpha_{rot}\beta_{cl}}{\beta_0}, \quad (2)$$

where $\beta_0 = \omega/c_0$ with c_0 is the low frequency, low amplitude speed of sound, and ω is the acoustic angular frequency in rad/sec. $\beta_{rot} = c_{rot}/c_0$ and $\beta_{cl} = c_{cl}/c_0$ are the scaled phase speed for translational and rotational relaxation respectively. β_{rot} and α_{rot} can be written in terms of the rotational relaxation collision number, where β_{cl} and α_{cl} are functions of Kn and are derived from the Navier-Stokes equations. The Navier-Stokes equations solution can be

written in terms of the complex classical propagation constant $K_{cl} = \alpha_{cl} + i\beta_{cl}$ and is given by the dispersion relation

$$\left(\frac{\omega}{c_0}\right)^2 + \left[1 + i\frac{\omega}{c_0^2}\left(\frac{4}{3}\frac{\mu}{\rho} + \frac{\kappa}{\rho c_v}\right)\right]K_{cl}^2 + \frac{\kappa}{\omega\rho c_v}\left(\frac{i}{\gamma} - \frac{4}{3}\frac{\omega\mu}{c_0^2\rho}\right)K_{cl}^4 = 0, \quad (3)$$

where μ is the coefficient of viscosity, κ is the coefficient of thermal conductivity, and c_v is the specific heat at constant volume.

At low frequencies, Eq (2) reduces to $\alpha_{cr} = \alpha_{cl} + \alpha_{rot}$ and all absorption mechanisms are additive. In that limit, α_{cl} becomes the familiar expression

$$\alpha_{cl} = \frac{\omega^2}{2\rho_0 c_0^3} \left(\frac{4}{3}\mu + \frac{(\gamma-1)\kappa}{c_p} \right). \quad (4)$$

It has been shown that the absorption due to vibrational relaxation is important to sound propagation on the Earth's atmosphere [9]. There have been many approaches for the theoretical development of absorption due to vibrational relaxation. The most common assumes the absorption due to a single relaxation process takes the form

$$\alpha_{relax} = \frac{\pi s}{c_0} \frac{\frac{f^2}{f_r}}{1 + \left(\frac{f}{f_r}\right)^2}, \quad (5)$$

where s is the relaxation strength and f_r is the frequency of maximum absorption due to the relaxation process, also called the relaxation frequency. While the development of Eq (5) relies on microscopic information of the internal structure of the molecules it is inherently a macroscopic relationship.

Comparison between the above theoretical predictions for the absorption of sound and experiment show poor agreement at high Kn due to the invalidity of the continuum assumption at high Kn . In addition, experimentation at high Kn is difficult [11] and is dependent on distance between source and receiver [15]. Several molecular-kinetics adjustments have been made to the theory to account for the the discrepancy at high Kn with varying degrees of success. Sutherland and Bass [12] use an empirical adjustment to account for the high Kn behavior while Buckner and Ferziger [13] and Sirovich and Thurber [14] use approximations to the Boltzmann equation to describe deviation from the Navier-Stokes prediction for a monatomic gas. These adjustments continue to be the standard treatment for modeling sound propagation at high Kn [12].

4. SIMULATION APPROACH

Since absorption mechanisms are inherently molecular properties, it is a natural progression to use a particle method for analysis. Because of the importance of relaxation effects on the absorption of sound, we were interested in investigating the relative importance of internal energy models as a function of Kn .

Acoustic waves were generated in the simulation domain by creating a piston boundary condition at one end of the domain. In all cases the velocity amplitude of the piston source is

20 m/s. Results for varying Kn were simulated in gaseous nitrogen as a hard sphere (molecular weight $M = 28.01$ and hard sphere diameter $\sigma = 3.78 \times 10^{-10}$ m). The variation in Kn was obtained by maintaining the cells per wavelength constant at 100, but varying the cell size from $1/2$ of a mean free path to $1/200$ of a mean free path. Each cell contained 50 particles per cell on average.

The time step was taken to be at least an order of magnitude smaller than the mean collision time and is on the order of picoseconds for each case. Care was taken that the time step remained smaller than the acoustic period of oscillation.

Calculations were performed at temperatures of 273 K, 2000 K, and 4000 K in order to monitor the temperature dependence of the excitation of the vibrational mode of nitrogen. Nitrogen's characteristic temperature was specified as 3371 K, and allows for a single vibrational model to adequately model the temperatures simulated (as shown in Figure 2). For the quantum model a single discrete vibrational level was simulated, while a single degree of freedom represented by two square terms is simulated in the classical model. For both cases nitrogen was modeled using two rotational degrees of freedom with each degree of freedom represented by a single square term.

Each case was initialized to start in thermal equilibrium, but since molecular relaxation is a disequilibrium process, we expect deviation from equilibrium. Section 5.2 describes this in further detail.

Dissociation of diatomic nitrogen in the high temperature-low pressure systems was found to be negligible for the conditions at which the simulations were run. An independent simulation was completed using DSMC in a single cell $1/30^{th}$ of a mean free path containing 25,000 N_2 molecules. This allowed for very similar temperatures and pressures to that of Case # in Section 5 which was determined to have the greatest likelihood for dissociation. Using a line-of-centers reaction model, the nitrogen molecules were given the opportunity to dissociate and was recorded if such an event occurred. The Arrhenius expression chosen to model the rate of dissociation was $k = 3.0 \times 10^{21} T^{-1.5} e^{-113,260/T} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ by Hammerling et al. [16]. The results were averaged over 20 ensembles to simulate a total of 500,000 molecules and recorded an average of 1449 dissociations over $7 \mu\text{s}$. It was determined that approximately 10,950 collisions were encountered between each dissociation. Based on the rate expression, the total simulation time and the pressure, Case # is predicted to have less than 1 molecule undergo dissociation over the entire simulation. This was validated with an independent DSMC simulation that allowed for dissociation modeled under very similar same conditions to that of Case # in Section 5.

A parallel, object-oriented DSMC solver was developed for this problem. The code was written in C++ and Message Passing Interface (MPI) for interprocessor communication, and was run on massively parallel computers. The object-oriented approach allows the DSMC algorithm to be divided into physical objects that are individually maintained. Cell and Particle classes were created to govern fundamental components of the algorithm. With this object oriented technique it was possible to develop a C++ code that was easy to read, maintain and modify. Despite excellent parallel efficiency, CPU time and memory requirements were quite large, taking approximately 6 hours on 32 processors for each run.

5. RESULTS

5.1. Absorption as a function of temperature

At low temperatures the quantum vibrational model will exhibit almost no vibrational activity as a large majority of diatomic nitrogen molecules will populate only the ground state given the high characteristic temperature. In contrast, the classical model allows for a continuous distribution of vibrational energy determined by the capacity of the molecule and energy available. At this low temperature, continuous and discrete vibrational models are expected to produce different results due to the contrasting behavior of the models. The classical harmonic oscillator model assumes a fully active vibrational mode while the quantum harmonic oscillator does not. At higher temperatures these models become more similar as excited states contain a much larger distribution of molecules.

The scaled absorption α/k_0 as a function of Kn is shown for 273 K, 2000 K and 4000 K in Figures 3, 4, and 5 respectively. DSMC results are also plotted against theoretical predictions given by Equations 2, 3, and 4. DSMC results for the discrete vibrational, classical vibration, and no vibration models are shown for a range of Kn in each case. The scaled absorption data was computed with two wavelengths worth of DSMC data for each case. Large deviations from continuum theory are seen for high Kn , as expected by the breakdown of the macroscopic model for $Kn > 0.05$. In each temperature case, differences between the models is small for low Kn . For Kn near the relaxation frequency, the amount of absorption depends more heavily on the vibrational model and temperature.

Due to the stochastic nature of DSMC, there is an intrinsic degree of scatter in the simulation results. This universal drawback of DSMC makes it difficult in certain cases to produce adequate resolution, and is a source of limitation for this work. Scatter is reduced by averaging many independent ensembles and random error is estimated from variance in repeated runs. As the temperature increases, the amount of scatter increases. The amount of random error was found to have no significant effect on the results shown for 273 K. However, for 2000 K and 4000 K the error is more significant. Error bars indicating one standard deviation are given for several simulations completed.

As the temperature increases, the excited state for discrete vibration becomes more populated. Therefore the differences between continuous and discrete vibrational models should become less, as is confirmed in Figures 4 and 5. It is difficult to determine more details for the higher temperatures due to the larger error.

5.2. Nonequilibrium

The physics of molecular relaxation imply that when a system that starts in equilibrium is subject to a sound source, then there is a time delay between the exchange in energy between translational and internal modes. The details of this relaxation process is shown in Figure 6 where the temperatures associated with the translational, rotational, and classical vibrational modes are specified for $Kn = 0.02$ at 273 K. The relaxation time for the classical vibrational model is considerably longer than that for rotation and is evident in minimal disturbance in the vibrational temperature.

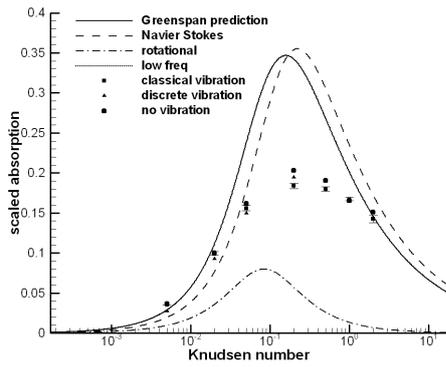


Figure 3. Scaled absorption in nitrogen for 273 K

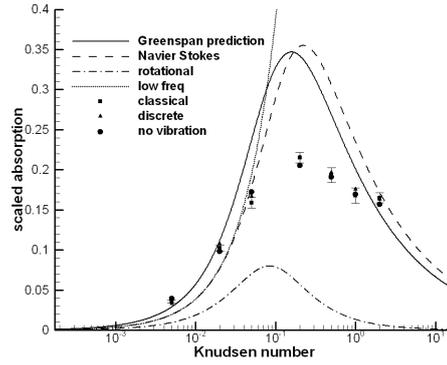


Figure 4. Scaled absorption in nitrogen for 2000 K

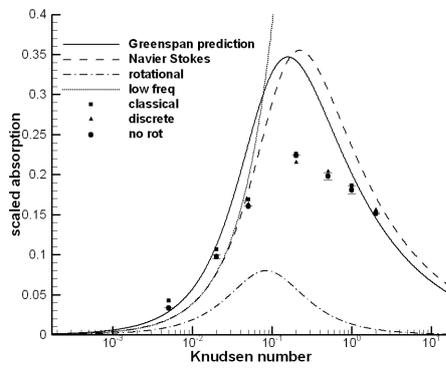


Figure 5. Scaled absorption in nitrogen for 4000 K

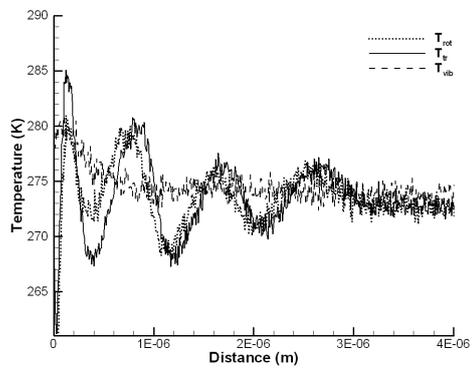


Figure 6. Nonequilibrium effects for $Kn = 0.02$ at 273 K

6. CONCLUSIONS

Given the particle nature of the direct simulation Monte Carlo method, it is possible to simulate the details of molecular relaxation with an acoustic source. Investigations with two fundamental internal energy models was performed as a function of Kn for multiple temperatures. Large deviations from continuum theory were seen for high Kn . Differences between internal energy modes were small for low Kn at low temperatures and for all Kn at high temperatures. Nonequilibrium effects were evident in the simulations, even at low Kn , because of the phenomenological nature of the internal energy models.

DSMC is a robust algorithm capable of simulating many systems. Despite large computation time, memory requirements and intrinsic scatter in the algorithm, DSMC is a powerful computational tool to study the importance of internal energy models on acoustic attenuation for a large range of Knudsen numbers.

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