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DSMC Simulation of Rayleigh-Brillouin Scattering in Binary Mixtures

Domenico Bruno^{1,a)}, Aldo Frezzotti^{2,b)} and Gian Pietro Ghioldi^{2,c)}

¹*Istituto di Nanotecnologia, Consiglio Nazionale delle Ricerche - Via G. Amendola, 122 - 70125 Bari, Italy*

²*Dipartimento di Scienze e Tecnologie Aerospaziali, Politecnico di Milano - Via La Masa, 34 - 20156 Milano, Italy.*

^{a)}domenico.bruno@cnr.it

^{b)}aldo.frezzotti@polimi.it

^{c)}gianpietro.ghioldi@polimi.it

Abstract. Rayleigh-Brillouin scattering spectra (RBS) in dilute gas mixtures have been simulated by the Direct Simulation Monte Carlo method (DSMC). Different noble gas binary mixtures have been considered and the spectra have been simulated adopting the hard sphere collision model. It is suggested that DSMC simulations can be used in the interpretation of light scattering experiments in place of approximate kinetic models. Actually, the former have a firmer physical ground and can be readily extended to treat gas mixtures of arbitrary complexity. The results obtained confirm the capability of DSMC to predict experimental spectra and clears the way towards the simulation of polyatomic gas mixtures of interest for actual application (notably, air) where tractable kinetic model equations are still lacking.

INTRODUCTION

Rayleigh-Brillouin scattering refers to the nonresonant scattering of light in a transparent medium. Density fluctuations cause fluctuations in the dielectric constant so that the medium acts like a diffraction grating. Equivalently, the process can be understood as the scattering of a photon by the phonons of the medium. In this picture, momentum and energy conservation require:

$$\mathbf{k}_{in} = \mathbf{k}_{out} + \mathbf{k}_{ph} \quad (1)$$

$$\omega_{in} = \omega_{out} + \omega_{ph} \quad (2)$$

where \mathbf{k} , ω are, respectively, the wavevector and the angular frequency of the participating waves. The spectrum of the scattered light therefore carries information on the propagation properties of the density fluctuations and is hence directly related to the thermodynamic and transport properties of the gas [1, 2].

The main parameter that characterizes light scattering in gases is the ratio between the probed wavelength and the mean free path in the gas. At small lengthscales, density perturbations do not propagate via collisions but via the particles free flight and the scattered light spectrum is determined only by the molecular velocity distribution and, at equilibrium, it is a simple Gaussian [3]. At large lengthscales, density perturbations are waves in a continuum medium. In this hydrodynamic limit, an analytical solution can be obtained from the Navier-Stokes equations [1, 2]. The same applies to gas mixtures [4], but now diffusion and thermal diffusion processes complicate the structure of the spectrum so that only in few limiting conditions the experiments can be exploited for the direct measurement of the diffusion and thermal diffusion coefficients [1, 2, 5].

Finally, in the kinetic regime, where the probed wavelength is comparable to the mean free path in the gas, no analytical solution is available and one has to resort to the solution of the Boltzmann equation [6].

Recently, light scattering in gases received renewed interest due to the possible applications of LIDAR (*Light Detection and Ranging*) to perform measurements of atmospheric properties remotely. We cite, in particular, the project to measure the wind speed distributions in the Earth atmosphere on a global scale by the ADM-Aeolus mission of the

European Space Agency (ESA) [7, 8, 9]. In general, experiments for remote atmospheric sensing detect the *backscattered* radiation (i.e. the scattering angle $\theta \approx \pi$) and fall in the gas kinetic regime [10].

Owing to the well known mathematical difficulties in solving the Boltzmann equation, interpretation of experimental spectra has been based on kinetic model equations [11, 12]. For one-component gases, the Tenti S6 model [11], consisting in a linear kinetic model for polyatomic gases constructed according to the Gross-Jackson systematic approximation [13], has been shown to reproduce experimental spectra with accuracy comparable to the experimental uncertainty [14, 10]. Model parameters are related to the gas transport properties. The model, however, cannot be used to describe gas mixtures; in addition, the value for the bulk viscosity coefficient cannot be obtained independently but it must be retrieved by fitting the model results to the experiment.

Light scattering experiments in gas mixtures have been done recently by Gu et al. [15] and previously by Letamendia et al. [16]. Kinetic models for monatomic gas mixtures of hard spheres or Maxwell's molecules have been used previously [5, 17] and recently a new model for mixtures of hard spheres [12] has been shown to provide good estimations of the scattering spectra of noble gas mixtures [15]. However, the underlying assumption of monoatomic particles prevents the application of such models to molecular gas mixtures. In order to interpret experiments in air, it has proved effective [10] to model air as a single polyatomic gas with effective thermodynamic and transport properties derived from the average properties of the mixture. This phenomenological approach has obvious limitations, in that it requires a priori knowledge of the mixture properties. Also, as it will become apparent in the following, the spectra for a gas mixture are not a linear superposition of those for the single species. The effectiveness of the phenomenological approach for air is to be found in the small relative difference between molecular properties (mass, polarizability, cross sections) of the mixture constituents and is therefore to be regarded as fortuitous and subject to validation in each particular case.

In order to overcome the limitations of available kinetic models, Direct Simulation Monte Carlo (DSMC) [18] has been proposed as a promising alternative. DSMC provides numerically accurate solutions of the full Boltzmann equation with no additional assumptions and model parameters are obtained from the system microscopic properties (interaction potentials or cross sections). In particular, DSMC reproduces the correct fluctuations spectra in single species monoatomic [19, 20] and polyatomic gases [21]. DSMC allows exploring the full range of Knudsen numbers, from the free molecular regime down to the hydrodynamic regime, although with increasing computational effort. It is worth noting that, even if DSMC and kinetic model equations have the same properties in the hydrodynamic limit, they may still show differences in the transition regime [22]. Therefore, it is interesting to investigate whether DSMC can provide an interpretation of light scattering experiments in mixtures. The approach could then be easily extended polyatomic gas mixtures.

In this work, equilibrium fluctuations in binary mixtures of monatomic gases are studied by DSMC simulations and the computed scattering spectra are compared with experimental light scattering data from Ref. [15].

RAYLEIGH-BRILLOUIN SCATTERING BASIC CONCEPTS

Rayleigh-Brillouin scattering is the nonresonant scattering of light by neutral particles [1, 2]. Incident light with wavevector \mathbf{k}_i is scattered by fluctuations in the refraction index, in turn caused by spontaneous density fluctuations. Scattered light is collected at an angle θ . The wavevector of the density fluctuation probed by the experiment is related to that of the incident light via the Bragg condition [1]:

$$k = 2k_i \sin \frac{\theta}{2} \quad (3)$$

The spectrum of the scattered light $I(R, \omega)$, collected at distance R from the interaction region as a function of the frequency difference between incident and scattered beams, is proportional to the generalized structure factor $S(\mathbf{k}, \omega)$ [1]:

$$I(R, \omega) = I_0 \frac{Nk_i^4}{32\pi^2} \frac{1}{R^2} \sin^2 \theta S(\mathbf{k}, \omega) \quad (4)$$

where N is the number of scatterers in the interaction region and I_0 is the intensity of the incident light.

$S(\mathbf{k}, \omega)$ is directly related to the Laplace-Fourier transform of the auto-correlation function of the dielectric constant fluctuation $\delta\epsilon$:

$$S(\mathbf{k}, \omega) = \text{Re} \{ \langle \delta\epsilon(\mathbf{k}, \omega) \delta\epsilon^*(\mathbf{k}, 0) \rangle \} \quad (5)$$

with:

$$\langle \delta\epsilon(\mathbf{k}, \omega) \delta\epsilon^*(\mathbf{k}, 0) \rangle = \int_0^\infty \int_V \int_V \langle \delta\epsilon(\mathbf{r} + \mathbf{r}', t) \delta\epsilon(\mathbf{r}', 0) \rangle e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} d\mathbf{r} d\mathbf{r}' dt \quad (6)$$

and where $\langle \delta\epsilon(\mathbf{r} + \mathbf{r}', t) \delta\epsilon(\mathbf{r}', 0) \rangle$ is the space-time correlation function of the dielectric fluctuations.

In gaseous binary mixtures the dielectric constant is in turn related to the fluctuations in the partial number densities n_i ($i = 1, 2$) through the Clausius-Mossotti relation [23]:

$$\delta\epsilon = \sum_{i=1}^2 \alpha_i \delta n_i \quad (7)$$

where α_i is the polarizability of the i -th species. Substituting Eq. (7) into Eq. (6) and Eq. (5) we obtain:

$$S(\mathbf{k}, \omega) = \sum_{i=1}^2 \sum_{j=1}^2 \alpha_i \alpha_j S_{ij}(\mathbf{k}, \omega) \quad (8)$$

where:

$$S_{ij}(\mathbf{k}, \omega) = \langle \delta n_i(\mathbf{k}, \omega) \delta n_j^*(\mathbf{k}, 0) \rangle. \quad (9)$$

In order to characterize the flow regime of the scattering process, it is useful to introduce the partial uniformity parameter y_i for each species composing the mixture:

$$y_i = \frac{1}{kl_i}, \quad i = 1, 2 \quad (10)$$

where l_i is the mean free path of the i -th species:

$$l_i = \left(\pi \sum_{j=1}^2 n_j d_{ij}^2 \sqrt{1 + m_i/m_j} \right)^{-1}, \quad i = 1, 2 \quad (11)$$

with m_i the atomic mass of the constituent i and d_{ij} the cross section diameter for collisions between particles of species i and j .

DSMC SIMULATION OF RBS SPECTRA

DSMC is a particle simulation method that solves the nonlinear Boltzmann equation. As such, it can simulate flows in the rarefied and/or hypersonic regime that cannot be dealt with in the framework of a fluid-dynamic treatment. The use of Monte Carlo particle methods for the study of hydrodynamic fluctuations in gases has been demonstrated by Malek Mansour et al. [19] who studied a non-equilibrium gas subject to a fixed heat flux. More recently, the authors have applied DSMC to the simulation of the light scattering spectra in Oxygen showing that DSMC gives accurate results [24]. A gas in thermal equilibrium is simulated and density fluctuations with respect to the equilibrium value, $\delta n_i = n_i - n_{i,0}$, are recorded for each species. δn_i is then doubly Fourier transformed in space and time, and squared to get a numerical estimation of the dynamic structure factor, $S(\mathbf{k}, \omega)$ [20]. For an isotropic medium, it is sufficient to simulate a one-dimensional spatial domain. The details of the molecular processes occurring in the gas system are specified by assigning the appropriate set of collision cross sections. Since the aim is to compare with experimental spectra obtained with noble gas mixtures [15], the hard sphere collision model is a simple and reasonable choice. For a binary mixture, three cross sections must be specified: the cross sections for collisions between equal particles d_{11} , d_{22} , and the cross section for mixed collisions, $d_{12} = d_{21}$. d_{ii} is chosen such that the accepted value for the shear viscosity of the pure gas (at a given temperature) is reproduced; d_{ij} is then computed as $d_{ij} = 1/2(d_{ii} + d_{jj})$. Alternatively, d_{ij} can be derived from measured diffusion coefficients.

Additional DSMC simulation parameters include the number of simulated particles, the collision cell spatial width and the timestep duration. They have been chosen according to the standard practice [18]. In particular, all simulations have been done using at least 3 cells for mean free path (the mixture mean free path being defined as $l = \sum_{i=1}^2 n_i/n l_i$) and with 30 particles per cell on average. The simulation domain has been set equal to 2 times the probed wavelength

and the number of points in space and time used to compute the spectra via FFT are 128 and 4096, respectively. In order to reduce the statistical scatter inherent in the method, results have been averaged over multiple ($2 - 8 \times 10^4$), statistically independent simulations of each experiment. Multiprocessor architecture is exploited by running each independent simulation on a single core. The typical computing time per core amounts to about 1.5 s on a Xeon[®] based workstation. The computational setting described above allows keeping the statistical relative error of computed spectra around 1%.

DESCRIPTION AND DISCUSSION OF RESULTS

The experimental spectra discussed in this work are described in Ref. [15]. The incoming laser has a wavelength $\lambda_i = 403 \text{ nm}$ and the scattered light is collected at an angle $\theta \approx 90^\circ$. Two binary mixtures of *He - Ar* and *He - Kr* are considered at different concentrations and pressures. The reference temperature for all the experiments is 297K. Table (1) reports the physical parameters characterizing the constituents of the mixtures; the hard sphere cross sections

TABLE 1. Physical parameters of the constituents of the mixtures

	Helium	Argon	Krypton
Particle Mass	$6.65 \times 10^{-27} \text{ Kg}$	$66.3 \times 10^{-27} \text{ Kg}$	$139.1 \times 10^{-27} \text{ Kg}$
Cross section diameter d_{ii}	$2.16 \times 10^{-10} \text{ m}$	$3.66 \times 10^{-10} \text{ m}$	$4.20 \times 10^{-10} \text{ m}$
Polarizability	$0.227 \times 10^{-40} \text{ Cm}^2 \text{ V}^{-1}$	$1.82 \times 10^{-40} \text{ Cm}^2 \text{ V}^{-1}$	$2.94 \times 10^{-40} \text{ Cm}^2 \text{ V}^{-1}$

for collisions between equal particles are desumed from the viscosities of the corresponding pure gases.

TABLE 2. Experimental Conditions. All the experiments are done at $T = 297 \text{ K}$.

Species 1	Species 2	p_1 (bar)	p_2 (bar)	y_1	y_2
Argon	Argon	1	1	1.32	1.32
Helium	Argon	1	1	0.54	1.63
Helium	Argon	2	2	1.08	3.28
Helium	Argon	1	3	1.16	2.96
Helium	Argon	3	1	1.00	3.59
Krypton	Krypton	0.65	0.65	1.13	1.13
Helium	Krypton	1.3	1.3	0.77	3.28
Helium	Krypton	2	2	1.17	5.01

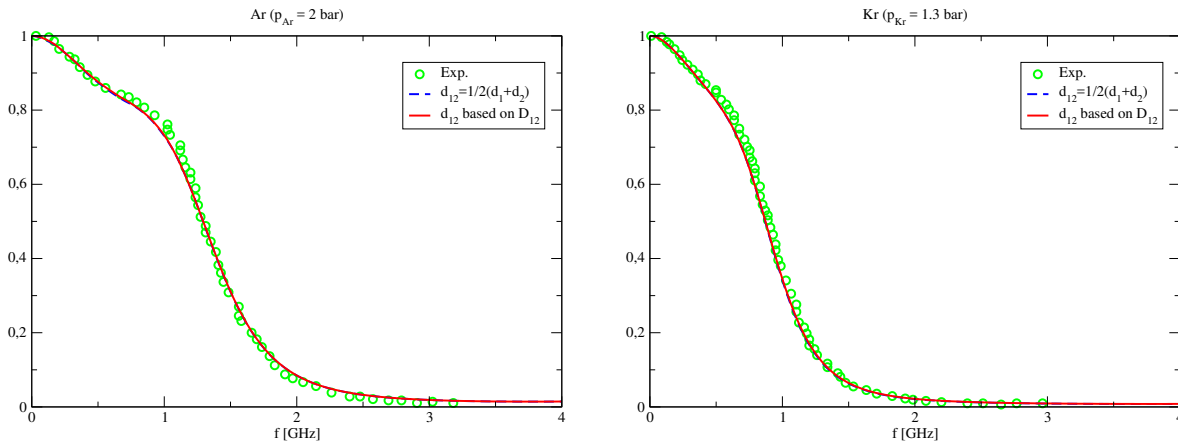


FIGURE 1. Comparison of experimental and calculated RBS spectra for pure Argon and pure Krypton.

Table (2) reports the partial pressures of each case with the corresponding uniformity parameters. As can be seen, all the experiments are conducted in the kinetic regime with the uniformity parameters that lie between 1 and 5. In order to compare the calculated spectra with the experimental data, the DSMC results have been convoluted with the instrument function described in Ref. [15]. For each experimental condition two different simulations have been done. One using the usual definition of the cross section between different species ($d_{ij} = d_{ji} = 1/2(d_{ii} + d_{jj})$) and the other using d_{ij} obtained from the diffusion coefficient.

Figures (1), (2), (3) compare the experimental data with the DSMC results. There is always good agreement, discrepancies being within few percent. The results obtained with the two different collision models also show very similar behaviour. Only in the case of the *He* – *Ar* mixture with $p_{He} = 1\text{bar}$ and $p_{Ar} = 3\text{bar}$ the discrepancies are somewhat larger. This result should be clarified and it will be the subject of future investigations.

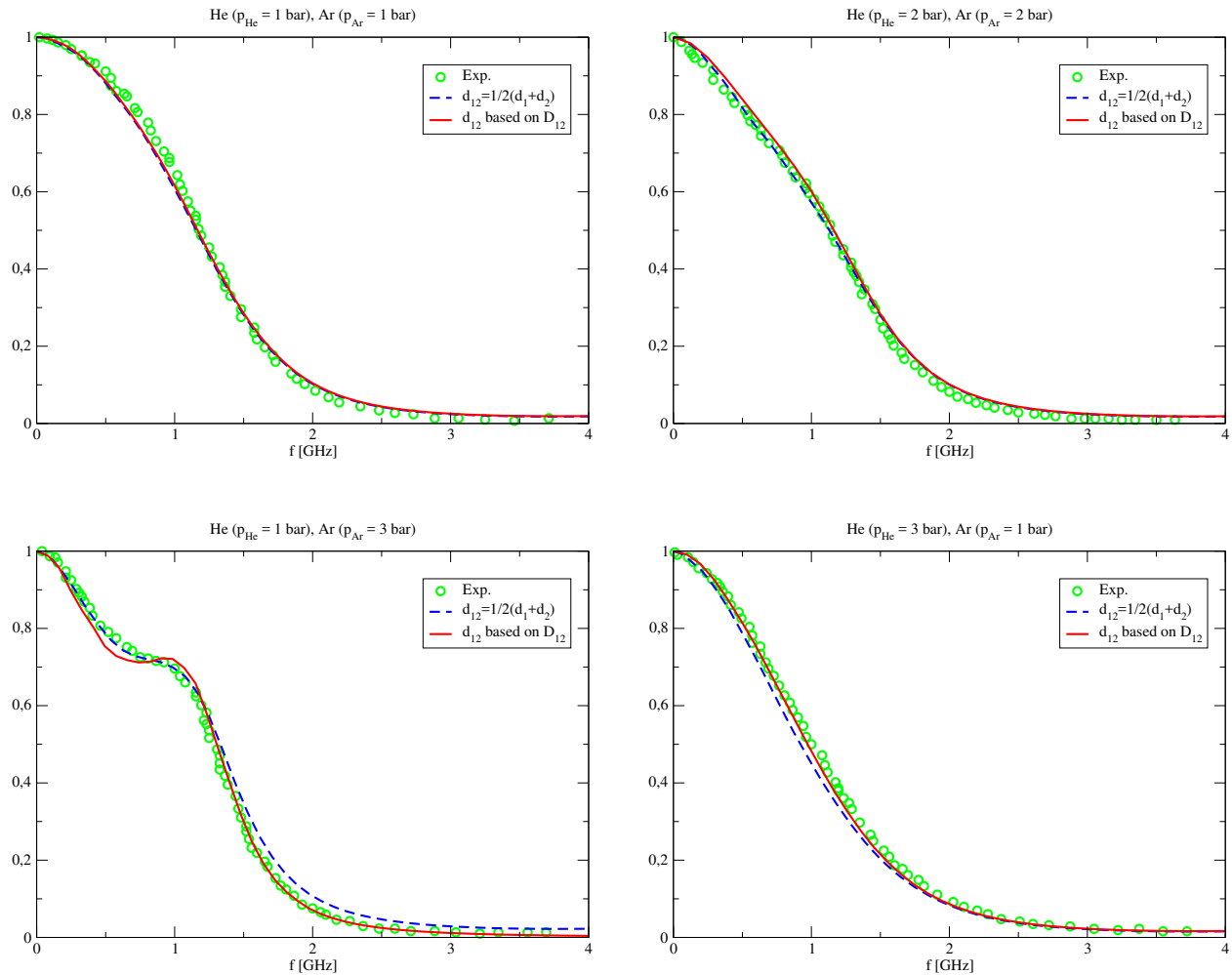


FIGURE 2. Comparison of experimental and calculated RBS spectra for two mixtures with different concentrations.

Figure (4) shows the effects of the presence of the light Helium particles on the heavier Argon and Krypton particles. In particular, the left panel of the Figure compares the spectrum of the mixture *He* – *Ar* with $p_{He} = 2\text{bar}$ and $p_{Ar} = 2\text{bar}$ with that obtained for pure Argon at $p_{Ar} = 2\text{bar}$. Since the polarizability of Helium is small compared to that of Argon ($\alpha_{He}/\alpha_{Ar} \approx 0.13$), and the spectra are proportional to the atomic polarizabilities squared (see eq. 8), the spectrum for the mixture is well approximated by the Argon spectrum alone. The results show that the presence

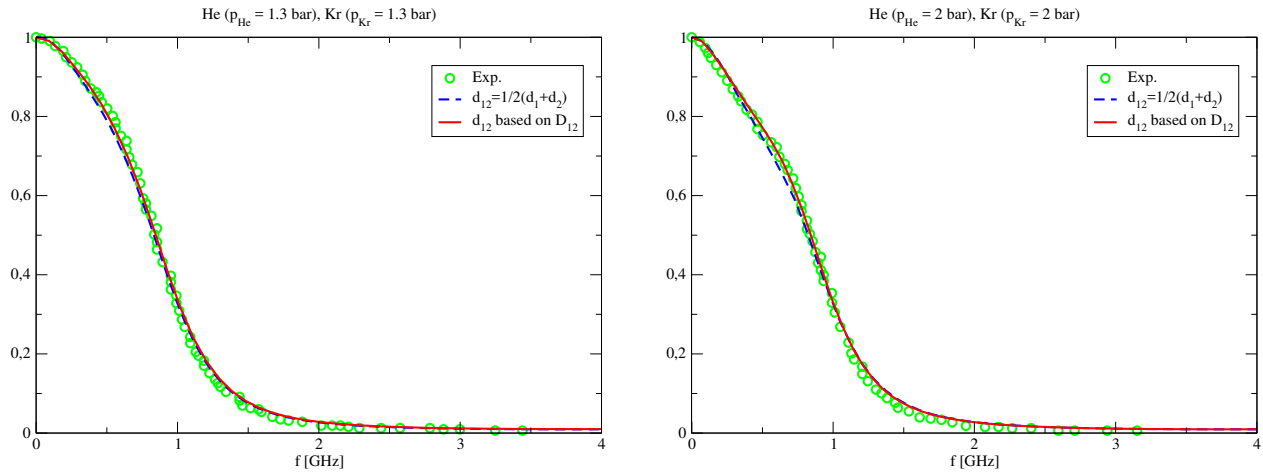


FIGURE 3. Comparison of experimental and calculated RBS spectra for two mixtures with different concentrations.

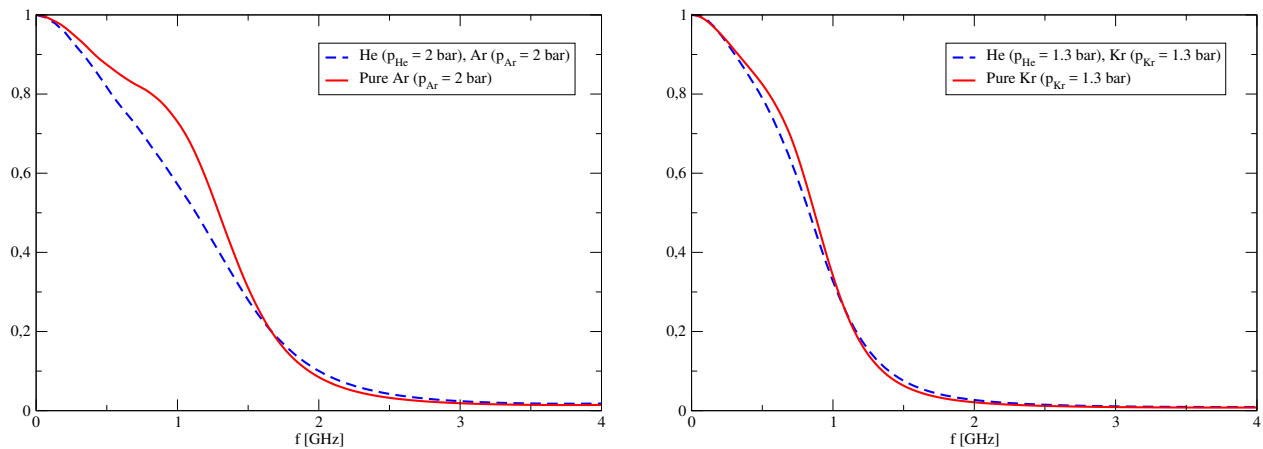


FIGURE 4. DSMC computed spectra obtained using the model $d_{ij} = 1/2(d_{ii} + d_{jj})$, $i \neq j$. Solid line: mixture results. Dashed line: single component results.

of light Helium particles changes significantly the spectrum of the Argon gas even if they do not contribute to the spectrum itself. The same analysis can be done also for the *He – Kr* mixture and pure Krypton in which the ratio $\alpha_{He}/\alpha_{Kr} \approx 0.07$ is even smaller. The right panel of the figure shows that in this case the two spectra are quite similar and the presence of Helium doesn't change significantly the results. This can be due to the much larger molecular weight of Kr particles with respect to Helium particles ($m_{Kr}/m_{He} \approx 21$).

The effects of the different molecular weights is presented in the left panel of Figure (5) in which two mixtures of *He – Ar* and *He – Kr* are compared at the same partial pressures. As can be seen the two spectra are quite different even if the partial pressures are the same. Although the cross sections diameters of the *Ar* and *Kr* atoms are similar but not equal, the differences can mainly be caused by the different molecular weights ($m_{Kr}/m_{Ar} \approx 2$). The right panel of Figure (5) shows the influence of different mole concentrations in the *He – Ar* mixture while keeping constant the total pressure at 4 bar. As can be seen there is a high sensitivity of the spectrum to the mole concentrations.

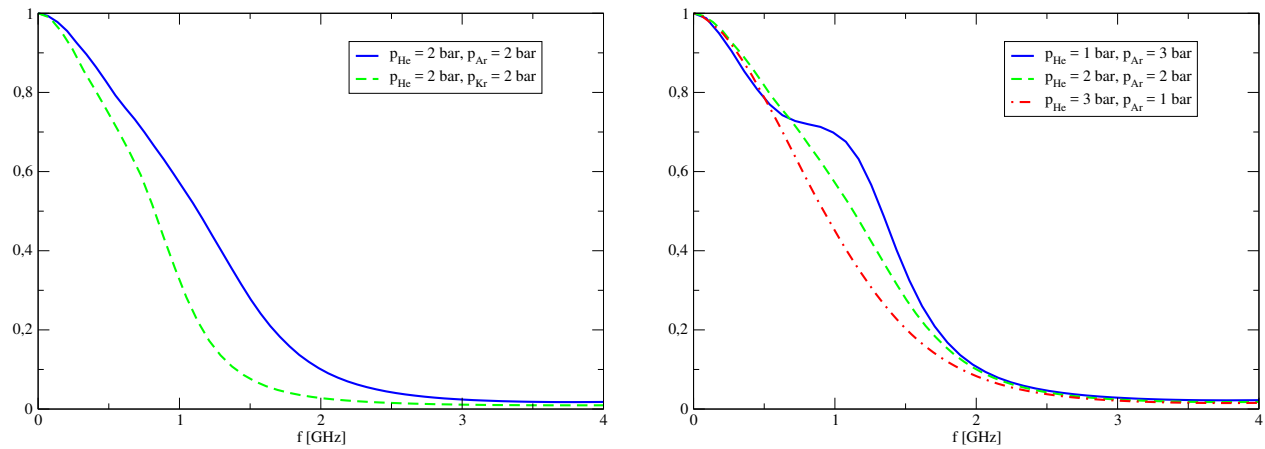


FIGURE 5. DSMC computed spectra obtained using the model $d_{ij} = 1/2(d_{ii} + d_{jj})$, $i \neq j$. Left panel: simulations at the same partial pressure but different constituents. Solid line: mixture of Helium and Argon. Dashed line: mixture of Helium and Krypton. Right panel: simulations at different partial pressures at constant total pressure ($p_{tot} = 4\text{bar}$) and same constituents (Helium and Argon).

CONCLUSIONS

Rayleigh-Brillouin scattering experiments in mixtures of noble gases have been simulated by DSMC solutions of the Boltzmann equation for a hard sphere gas. Two different cross section models for collisions between different particles have been adopted in order to verify the sensitivity of the spectra to the models. All the adopted models reproduce the experimental data of Ref. [15] with accuracy comparable to the experimental uncertainty. The results confirm again the capability of the DSMC method to correctly reproduce the dynamics of gas mixtures (at least for mixtures of noble gases) using a limited number of adjustable parameters. These encouraging results push for future studies of light scattering in polyatomic gas mixtures where tractable kinetic models are not yet available.

REFERENCES

- [1] B. Berne and R. Pecora, *Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics*, Dover Books on Physics Series (Dover Publications, 1976).
- [2] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (Dover Books on Physics, 1980).
- [3] L. D. Landau and E. M. Lifshitz, *Statistical Physics (Part 1)* (Butterworth-Heinemann, 1980) Chap. Spatial correlation of density fluctuations., pp. 350–353.
- [4] C. Cohen, J. W. H. Sutherland, and J. M. Deutch, *Physics and Chemistry of Liquids* **2**, 213–235 (1971), <http://dx.doi.org/10.1080/00319107108083815>.
- [5] N. A. Clark, *Phys. Rev. A* **12**, 2092–2105 Nov (1975).
- [6] C. Cercignani, *The Boltzmann Equation and Its Applications* (Springer-Verlag, Berlin, 1988).
- [7] A. Stoffelen, G. J. Marseille, F. Bouttier, D. Vasiljevic, S. de Haan, and C. Cardinali, *Quarterly Journal of the Royal Meteorological Society* **132**, 1927–1947 (2006).
- [8] A. Ansmann, U. Wandinger, O. L. Rille, D. Lajas, and A. G. Straume, *Appl. Opt.* **46**, 6606–6622 Sep (2007).
- [9] O. Reitebuch, C. Lemmerz, E. Nagel, U. Paffrath, Y. Durand, M. Endemann, F. Fabre, and M. Chaloupy, *Journal of Atmospheric and Oceanic Technology* **26**, 2501–2515 (2009).
- [10] Z. Gu and W. Ubachs, *The Journal of Chemical Physics* **141**, p. 104320 (2014).
- [11] G. Tenti, C. Boley, and R. Desai, *Can. J. Phys.* **52**, p. 285 (1974).
- [12] J. R. Bonatto and W. Marques, Jr, *Journal of Statistical Mechanics: Theory and Experiment* **9**, p. P09014 (2005).
- [13] E. P. Gross and E. A. Jackson, *Physics of Fluids* **2**, 432–441 (1959).
- [14] M. O. Vieitez, E. J. van Duijn, W. Ubachs, B. Witschas, A. Meijer, A. S. de Wijn, N. J. Dam, and W. van de Water, *Physical Review A* **82**, p. 043836 October (2010).

- [15] Z. Gu, W. Ubachs, W. Marques, and W. van de Water, [Phys. Rev. Lett.](#) **114**, p. 243902Jun (2015).
- [16] L. Letamendia, J. P. Chabrat, G. Nouchi, J. Rouch, C. Vaucamps, and S.-H. Chen, [Phys. Rev. A](#) **24**, 1574–1590Sep (1981).
- [17] C. Boley and S. Yip, *Journal de Physique Colloques* **33**, 43–49 (1972).
- [18] G. A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Clarendon Press, Oxford, 1994).
- [19] M. M. Mansour, A. L. Garcia, G. C. Lie, and E. Clementi, [Physical Review Letters](#) **58**, 874–877 (1987).
- [20] D. Bruno, M. Capitelli, S. Longo, and P. Minelli, [Chemical Physics Letters](#) **422**, 571–574May (2006).
- [21] D. Bruno, A. Frezzotti, and G. P. Ghiroldi, [Physics of Fluids \(1994-present\)](#) **27**, p. 057101May (2015).
- [22] C. Tantos, D. Valougeorgis, and A. Frezzotti, [International Journal of Heat and Mass Transfer](#) **88**, 636–651 (2015).
- [23] P. Atkins and J. de Paula, *Atkins' Physical Chemistry* (Oxford University Press, 2010).
- [24] D. Bruno, A. Frezzotti, and G. Ghiroldi, Submitted (2016).
- [25] D. Bruno, M. Capitelli, F. Esposito, S. Longo, and P. Minelli, [Chemical Physics Letters](#) **360**, 31–37 (2002).
- [26] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, 1995).
- [27] C. Borgnakke and P. S. Larsen, [J. Comput. Phys.](#) **18**, 405–420 (1975).