

Models for Bulk Viscosity in Carbon Dioxide

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Abstract. Bulk viscosity in carbon dioxide is studied using the accurate kinetic theory method. Complex structure of the CO₂ molecule and various channels for vibrational relaxation are taken into account while calculating the vibrational relaxation time. It is shown that in the general case, the bulk viscosity coefficient cannot be represented as a sum of independent contributions of rotational and vibrational degrees of freedom. The predicted ratio of bulk and shear viscosity coefficients does not exceed 5 for temperatures lower than 2000 K. Thus we put in question the widely used assumption about the high ratio of bulk and shear viscosity coefficients in CO₂ at low temperature.

INTRODUCTION

The present study is devoted to the bulk viscosity in carbon dioxide. Bulk viscosity characterizes the finite time of energy exchange between the translational and internal degrees of freedom, and contributes to the normal mean stress. A number of scientific teams are engaged in experimental [1, 2, 3, 4] and theoretical [5, 6, 7, 8, 9, 10, 11, 12, 13] studies of bulk viscosity. Of special interest is evaluation of bulk viscosity in CO₂; its complex molecular structure and multiple internal energy relaxation mechanisms [14, 15, 16] may significantly affect the transport properties.

Until recently, the bulk viscosity was systematically neglected in the computational fluid dynamics. A few years ago, in the work [17] it was shown that at room temperature, the bulk viscosity in carbon dioxide can be hundreds and thousands of times larger than the shear viscosity, and, as a consequence, provide a large contribution to the normal stress. This assumption was used in [18] for studying the shock wave structure, and some interesting features of the fluid-dynamic variable profiles are found. On the other hand, in [19, 20] these results were not confirmed. Thus, at the moment there is an uncertainty in the data on bulk viscosity in CO₂.

The aim of the present work is to obtain, using kinetic theory methods, reliable information on the bulk viscosity in carbon dioxide under various conditions. The bulk viscosity is calculated taking into account coupled vibrational modes of CO₂ as well as complex mechanisms of vibrational relaxation including intra- and inter-mode vibrational energy transitions. Chemical reactions are not included to the kinetic scheme since we are interested in the single-component gas properties. The modified Chapman–Enskog method in the one-temperature approximation is applied to derive the theoretical model; some approximations are introduced to obtain preliminary quantitative results. The results are compared to those obtained in [17]; the contributions of rotational and vibrational degrees of freedom to the bulk viscosity are evaluated.

KINETIC MODEL

In the one-temperature kinetic theory approach, the following relation between characteristic times of processes holds [9]:

$$\tau_{tr} < \tau_{rot} < \tau_{vibr} \ll \theta, \quad (1)$$

here τ_{tr} , τ_{rot} , τ_{vibr} are the characteristic times of translational, rotational and vibrational energy exchanges respectively, θ is the macroscopic time.

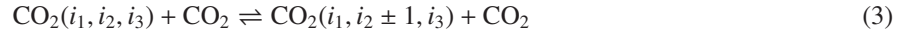
CO₂ is a linear triatomic molecule [21] which, in the ground electronic state, has three vibrational degrees of freedom. The first mode is the symmetric stretching mode with the frequency ν_1 , the second one is the doubly degenerated bending mode (ν_2), and the third mode is the asymmetric stretching mode (ν_3). The corresponding vibrational quantum numbers are i_1, i_2, i_3 .

For anharmonic oscillators, the modes are coupled, and the vibrational energy $\varepsilon_{i_1, i_2, i_3}$ is introduced by the following formula [21]:

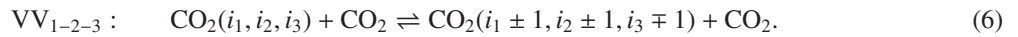
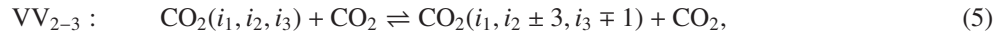
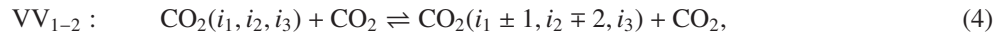
$$\frac{\varepsilon_{i_1, i_2, i_3}}{hc} = \sum_{m=1}^3 \omega_m^e \left(i_m + \frac{d_m}{2} \right) + \sum_{m=1}^3 \sum_{n \geq m}^3 x_{mn}^e \left(i_m + \frac{d_m}{2} \right) \left(i_n + \frac{d_n}{2} \right) + \dots, \quad (2)$$

here h is the Plank constant, c is the speed of light, ω_m^e , x_{mn}^e are the spectroscopic constants, d_m is the degeneracy of the m -th mode, $d_1 = d_3 = 1$, $d_2 = 2$. The rotational energy of the linear molecule is described similarly to that of diatomic species.

Rapid inelastic processes leading to the internal energy relaxation and thus responsible for the effect of bulk viscosity are the rotational and vibrational energy exchanges. Multiple channels of vibrational relaxation are possible in carbon dioxide: VV and VT exchanges within modes as well as inter-mode transitions [14]. Analysis of various mechanisms performed in [20] shows that the dominant channels are: VT₂ vibrational–translational exchange in the bending mode



(a partner in a collision does not change its internal state), and several VV _{$m-k$} vibrational transitions between different modes



Whereas two-quantum transitions (4) are almost resonant and therefore cannot significantly affect the bulk viscosity, other inter-mode transitions may give a noticeable contribution to this transport property.

BULK VISCOSITY CALCULATION

Under condition (1), the pressure tensor \mathbf{P} in the first-order approximation of the Chapman–Enskog method is expressed as [9]

$$\mathbf{P} = (p - p_{\text{rel}}) \mathbf{I} - 2\eta \mathbf{S} - \zeta \nabla \cdot \mathbf{v} \mathbf{I},$$

where \mathbf{S} is the traceless strain rate tensor, \mathbf{I} is the unit tensor, η , ζ are the coefficients of shear and bulk viscosity, p_{rel} is the relaxation pressure.

We use the first-order approximation of the modified Chapman–Enskog method to calculate the transport coefficients; the algorithm is discussed in details in [9]. In particular, the Sonine and Waldmann–Trübenbacher polynomial expansions in velocities and internal energies are used to express the transport coefficients as solutions of linear algebraic systems; the coefficients of linear systems are the bracket integrals depending on the cross sections of rapid processes [9].

The shear η and bulk viscosity ζ coefficients for a single-component gas in the one-temperature approach are obtained in the form [9]:

$$\eta = \frac{5kT}{8\Omega^{(2,2)}}, \quad \zeta = \frac{kT}{\beta_{\text{int}}} \left(\frac{c_{\text{int}}}{c_V} \right)^2, \quad (7)$$

$\Omega^{(2,2)}$ is the collision integral calculated using [22], k is the Boltzmann constant, T is the gas temperature, β_{int} is the bracket integral associated to the internal energy variation in rapid inelastic collisions, $c_V = c_{\text{tr}} + c_{\text{rot}} + c_{\text{vibr}} = c_{\text{tr}} + c_{\text{int}}$ is the total specific heat at constant volume, c_{tr} , c_{rot} and c_{vibr} are the components of the specific heat corresponding to the translational, rotational and vibrational energy,

$$c_{\text{tr}} = \left(\frac{\partial E_{\text{tr}}}{\partial T} \right)_V = \frac{3k}{2m}, \quad c_{\text{rot}} = \left(\frac{\partial E_{\text{rot}}}{\partial T} \right)_V = \frac{k}{m}, \quad c_{\text{vibr}} = \left(\frac{\partial E_{\text{vibr}}}{\partial T} \right)_V, \quad (8)$$

m is the molecular mass, E_{tr} , E_{rot} , E_{vibr} are the translational, rotational and vibrational energies per unit mass. While the rotational and translational components of the total specific heat are assumed to be constant, the vibrational one is calculated explicitly using the definition of specific vibrational energy. The vibrational energy per unit mass E_{vibr} is introduced by the formula

$$E_{vibr} = \frac{1}{mZ_{vibr}} \sum_{i_1, i_2, i_3} (i_2 + 1) \varepsilon_{i_1, i_2, i_3} \exp\left(-\frac{\varepsilon_{i_1, i_2, i_3}}{kT}\right), \quad (9)$$

Z_{vibr} is the vibrational partition function

$$Z_{vibr} = \sum_{i_1, i_2, i_3} (i_2 + 1) \exp\left(-\frac{\varepsilon_{i_1, i_2, i_3}}{kT}\right), \quad (10)$$

$i_2 + 1$ is the statistical weight of the bending mode (for other modes the vibrational statistical weight is unit).

The integral bracket β_{int} characterizes the averaged variation of internal energy in the most frequent inelastic collisions [9]

$$\beta_{int} = 2 \left\langle (\Delta \mathcal{E}^{int})^2 \right\rangle. \quad (11)$$

Here, the dimensionless variation of the internal energy is given by

$$\Delta \mathcal{E}^{int} = \frac{\varepsilon_{i'_1 i'_2 i'_3} + \varepsilon_{j'} + \varepsilon_{k'_1 k'_2 k'_3} + \varepsilon_{l'} - \varepsilon_{i_1 i_2 i_3} - \varepsilon_j - \varepsilon_{k_1 k_2 k_3} - \varepsilon_l}{kT} = \frac{\varepsilon_{i' j'} + \varepsilon_{k' l'} - \varepsilon_{ij} - \varepsilon_{kl}}{kT} = \Delta \mathcal{E}^{rot} + \Delta \mathcal{E}^{vibr}, \quad (12)$$

ε_j is the rotational energy at the level j , primed subscripts correspond to the energies after collision. In the notation ε_{ij} for the internal energy, the notation i for the vibrational state is used for the convenience instead of the set of quantum numbers (i_1, i_2, i_3) . In this study, the rigid rotator model is used for the rotational energy; this allows us to split the energy variation to two terms corresponding to the rotational and vibrational energy.

The averaging operator is introduced on the basis of the zero-order distribution function, which in the one-temperature approach represents the Maxwell–Boltzmann distribution over velocity and internal energy [9]

$$\left\langle (\Delta \mathcal{E}^{int})^2 \right\rangle = \left(\frac{kT}{\pi m} \right)^{1/2} \sum_{ijkl i' j' k' l'} \frac{s_{ij} s_{kl}}{Z_{int}^2} \int (\Delta \mathcal{E}^{int})^2 \gamma^3 \exp\left(-\gamma^2 - \frac{\varepsilon_{ij}}{kT} - \frac{\varepsilon_{kl}}{kT}\right) \sigma_{ijkl}^{i' j' k' l'} d^2 \Omega d\gamma. \quad (13)$$

Here $s_{ij} = s_i s_j = (i_2 + 1)(2j + 1)$ is the internal statistical weight, Z_{int} is the internal partition function; for rigid rotators $Z_{int} = Z_{vibr} Z_{rot}$, γ is the dimensionless relative velocity, $\sigma_{ijkl}^{i' j' k' l'}$ is the differential cross section of an inelastic collision resulting in the internal energy variation, $d^2 \Omega$ is the solid angle.

On the basis of Eq. (13), the internal energy relaxation time can be introduced [23, 5, 9]:

$$\frac{1}{\tau_{int}} = \frac{kn}{mc_{int}} \beta_{int}, \quad (14)$$

and the expression for the bulk viscosity coefficient takes the form

$$\zeta = \frac{k^2 T n}{m} \left(\frac{c_{int}}{c_v} \right)^2 \frac{\tau_{int}}{c_{int}} = \frac{R c_{int}}{c_v^2} p \tau_{int}, \quad (15)$$

$R = k/m$ is the gas constant.

Usually in experiments, instead of the internal energy relaxation time, the rotational τ_{rot} and vibrational τ_{vibr} relaxation times are measured. Therefore it is useful to express the bulk viscosity coefficient in terms of τ_{rot} , τ_{vibr} . For this purpose, some additional assumptions are required. If, following to Mason and Monchick [23], we assume that collisions with simultaneous exchanges of rotational and vibrational energy are rare, then the collision cross sections for vibrational energy transitions do not depend on the rotational states $\sigma_{vibr} = \sigma_{ik}^{i' k'}$, and vice versa, $\sigma_{rot} = \sigma_{jl}^{j' l'}$. This allows splitting the integral in Eq. (13) to two terms connected with the rotational $(\Delta \mathcal{E}^{rot})^2$ and vibrational $(\Delta \mathcal{E}^{vibr})^2$ energy variations. Note that under above assumption, the integral of $\Delta \mathcal{E}^{rot} \Delta \mathcal{E}^{vibr} = 0$. Then the bracket integral $\beta_{int} = \beta_{rot} + \beta_{vibr}$, and the internal energy relaxation time can be written as

$$\frac{c_{int}}{\tau_{int}} = \frac{c_{rot}}{\tau_{rot}} + \frac{c_{vibr}}{\tau_{vibr}}. \quad (16)$$

Finally the bulk viscosity coefficient is obtained in the following form:

$$\zeta = pR \left(\frac{c_{\text{int}}}{c_V} \right)^2 \left(\frac{c_{\text{rot}}}{\tau_{\text{rot}}} + \frac{c_{\text{vibr}}}{\tau_{\text{vibr}}} \right)^{-1}. \quad (17)$$

It is worth mentioning that, in the well known work by Cramer [17], the bulk viscosity coefficient is split a priori to two independent contributions,

$$\zeta = \zeta^{\text{rot}} + \zeta^{\text{vibr}}, \quad (18)$$

and each coefficient is associated to the corresponding relaxation time:

$$\zeta^{\text{rot}} = \left(\frac{R}{c_V} \right)^2 p \tau_{\text{rot}}, \quad \zeta^{\text{vibr}} = \frac{R c_{\text{vibr}}}{c_V^2} p \tau_{\text{vibr}}, \quad (19)$$

(it is assumed that $c_{\text{rot}} = R$). It is evident that Eqs. (18), (19) do not follow from Eq. (17). The validity of the assumption (18) is discussed in the next section.

RESULTS AND DISCUSSION

Let us discuss first the relaxation times of rotational and vibrational energy. The rotational relaxation time is computed according to the Parker model [24], under assumption that τ_{rot} does not depend on the vibrational spectrum of the molecule. Calculation of vibrational relaxation time in CO_2 is a more complicated problem due to multiple relaxation channels (3)–(6). Available experimental data exist only for particular relaxation processes [25]. To calculate the overall vibrational relaxation time we propose the following algorithm. We define τ_{vibr} as a result of all collisions leading to the vibrational energy variation

$$\frac{1}{\tau_{\text{vibr}}} = \frac{2kn}{mc_{\text{vibr}}} \left\langle (\Delta \mathcal{E}^{\text{vibr}})^2 \right\rangle. \quad (20)$$

Assuming that the cross sections of vibrational energy transitions are independent of the rotational states, after some transformations we obtain:

$$\left\langle (\Delta \mathcal{E}^{\text{vibr}})^2 \right\rangle = \left(\frac{kT}{\pi m} \right)^{1/2} \sum_{ik'i'k'} \frac{(i_2 + 1)(k_2 + 1)}{Z_{\text{vibr}}^2} \int (\Delta \mathcal{E}^{\text{vibr}})^2 \gamma^3 \exp \left(-\gamma^2 - \frac{\varepsilon_i}{kT} - \frac{\varepsilon_k}{kT} \right) \sigma_{ik}^{i'k'} d^2 \Omega d\gamma. \quad (21)$$

In this expression, we make summation over all the vibrational states of reagents and products, $\Delta \mathcal{E}^{\text{vibr}}$ includes contribution of VT_2 and VV_{m-k} transitions (3)–(6). Other assumptions introduced to calculate this integral: the cross sections of vibrational energy transitions are calculated as elastic collision cross sections multiplied by the corresponding transition probabilities; elastic collisions are described using the hard sphere model. Thus we obtain the analytical formula depending on the transition probabilities. The probabilities of VT and VV_{m-k} transitions are calculated using the SSH-theory [26].

Since the number of vibrational transitions in the CO_2 molecule is about 10^6 (see [15]), direct summation in (21) requires significant computational efforts. For the preliminary estimates of the relaxation time we take into account only transitions between the lowest vibrational states:

$$\text{VT}_2 : \quad (0, 1, 0) \rightleftharpoons (0, 0, 0), \quad (0, 2, 0) \rightleftharpoons (0, 1, 0), \quad (0, 3, 0) \rightleftharpoons (0, 2, 0); \quad (22)$$

$$\text{VV}_{1-2} : \quad (1, 0, 0) \rightleftharpoons (0, 2, 0), \quad (1, 1, 0) \rightleftharpoons (0, 3, 0); \quad (23)$$

$$\text{VV}_{2-3} : \quad (0, 0, 1) \rightleftharpoons (0, 3, 0); \quad (24)$$

$$\text{VV}_{1-2-3} : \quad (0, 0, 1) \rightleftharpoons (1, 1, 0). \quad (25)$$

Although such an approximation may cause some lost of accuracy, it provides fast and efficient qualitative estimates for the vibrational relaxation times. In our future works we are planning to take into account all vibrational transitions. We expect that it will lead to monotonic behavior of the vibrational relaxation times as well as ζ_{vibr} .

In Figure 1, the vibrational relaxation time calculated as a function of temperature T using Eq. (20) is compared with the VT_2 relaxation time measured experimentally [25]. Comparison of τ_{vibr} and τ_{VT_2} shows a satisfactory agreement. At low temperatures, τ_{vibr} and τ_{VT_2} are very close. However, it is interesting to note that the overall relaxation time τ_{vibr} is non-monotonic with temperature. A similar effect has been pointed out in recent works on the vibrational relaxation in diatomic species, both in experiments [27] and high-fidelity quasi-classical trajectory calculations [28]. The reason for such behaviour in polyatomic gases can be a competing effects of various transitions at different temperatures; for VV and VT exchanges probabilities increase with different rates. To assess the influence of excited vibrational states on τ_{vibr} we plan to study the vibrational relaxation time taking into account more vibrational states and transitions.

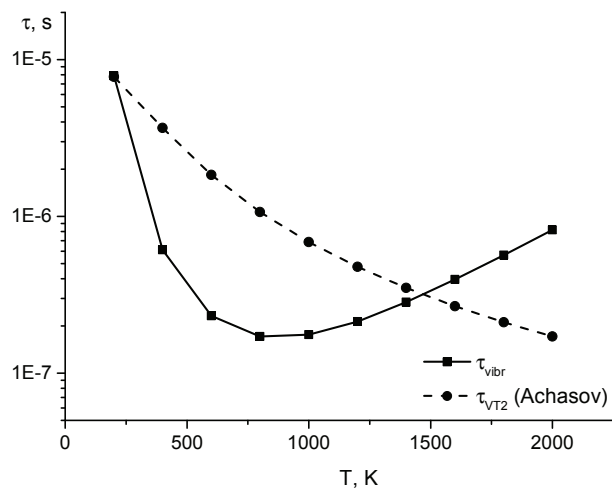


FIGURE 1. Characteristic times for CO_2 . Comparison of τ_{vibr} calculated using the kinetic theory with τ_{VT_2} measured experimentally [25].

In Figure 2, the rotational and vibrational relaxation times are compared with the internal energy relaxation time τ_{int} calculated using Eq. (16). One can notice that the temperature dependence of τ_{int} is similar to that of τ_{rot} whereas τ_{vibr} is significantly higher, especially for low temperatures.

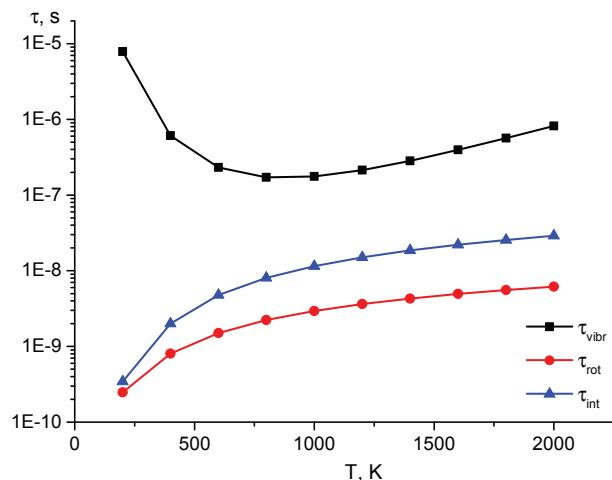


FIGURE 2. Characteristic times for CO_2 . Comparison of τ_{vibr} , τ_{rot} and τ_{int} calculated using the kinetic theory.

Now let us consider the bulk viscosity coefficients. To compare our results with those of Cramer [17], we cal-

culated ζ as well as two independent contributions ζ_{rot} and ζ_{vibr} given by Eq. (19) and their sum (18). In Figure 3 (left graph), we compare the ratio $(\zeta_{\text{vibr}} + \zeta_{\text{rot}})/\eta$ obtained using different data for the vibrational relaxation time. At $T > 1000$ K, the agreement with Cramer's results is very close. At low temperatures, there is a discrepancy caused by different models for the relaxation times; the results of Cramer are based on the experiments of Simpson [29] whereas we use both theoretical formula (20) and experiments from [25].

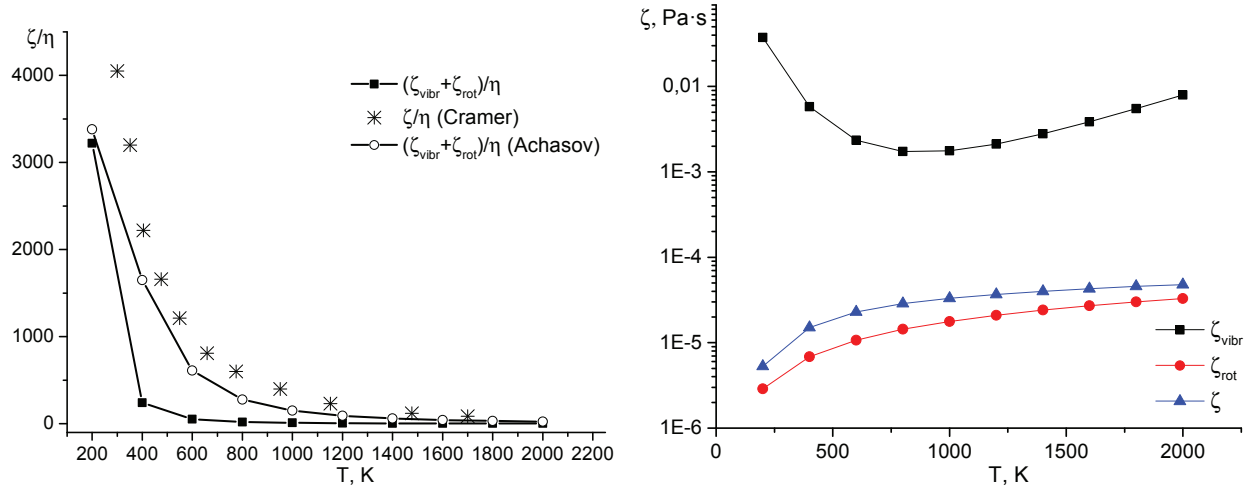


FIGURE 3. Temperature dependence of ζ/η (left) and bulk viscosity coefficients (right) for CO_2 .

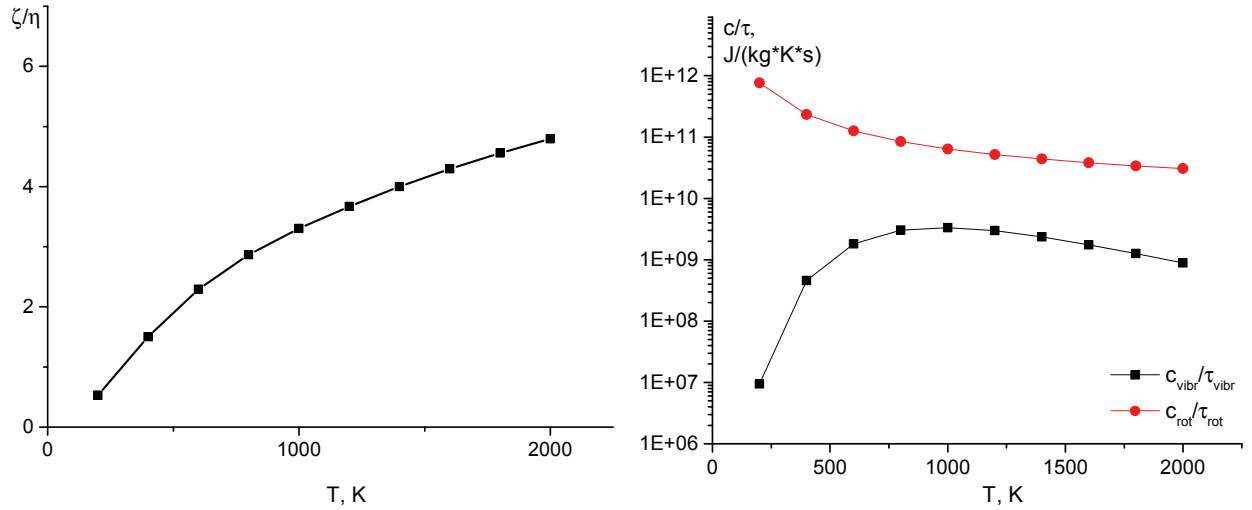


FIGURE 4. Temperature dependence of ζ/η (left) and $c_{\text{rot}}/\tau_{\text{rot}}$, $c_{\text{vibr}}/\tau_{\text{vibr}}$ (right) for CO_2 .

It has to be noted that in the Cramer's formulation, the main contribution to the bulk viscosity at low temperatures is given by the vibrational degrees of freedom. In Figure 3 (right graph), we compare ζ_{rot} and ζ_{vibr} using the logarithmic scale. One can see that ζ_{vibr} is several orders of magnitude greater than ζ_{rot} ; therefore their sum is basically independent of the rotational degrees of freedom. Nevertheless, if we calculate ζ using the accurate kinetic theory formulation (17) (the blue curve), we see that the main role belongs to rotations. It is not surprising since at low temperatures, vibrational degrees of freedom can be treated as frozen compared to rotational. It should be noted that in the case $\tau_{\text{vibr}} \gg \tau_{\text{rot}}$, vibrational relaxation cannot be described in the frame of the one-temperature model assuming weak deviation from equilibrium; on the contrary, slow relaxation processes have to be described using the relaxation equations derived

under strongly non-equilibrium conditions.

In Figure 4 (left), the ratio ζ/η calculated using the kinetic theory model (17) is given in the linear scale. Contrarily to the results of [17], the ratio increases with T and does not exceed 5 at $T = 2000$ K. In Figure 4 (right), we compare the ratios $c_{\text{rot}}/\tau_{\text{rot}}$ and $c_{\text{vibr}}/\tau_{\text{vibr}}$ which specify the contributions of corresponding degrees of freedom to the bulk viscosity (17). At low temperatures, $c_{\text{rot}}/\tau_{\text{rot}}$ is much greater than $c_{\text{vibr}}/\tau_{\text{vibr}}$. With rising T , c_{vibr} increases considerably whereas c_{rot} remains constant, and the values $c_{\text{rot}}/\tau_{\text{rot}}$, $c_{\text{vibr}}/\tau_{\text{vibr}}$ become closer. However, the vibrational relaxation time given by Eq. (20) also increases, faster than c_{vibr} ; this yields almost constant difference between $c_{\text{rot}}/\tau_{\text{rot}}$ and $c_{\text{vibr}}/\tau_{\text{vibr}}$ with further temperature increase. Finally, we conclude that the contribution of vibrational modes to the bulk viscosity is about one order of magnitude lower compared to that of rotational degrees of freedom.

CONCLUSIONS

Two models for the bulk viscosity coefficient in carbon dioxide are discussed: the one based on the accurate kinetic theory methods as well as the simplified formulation representing the bulk viscosity coefficient as a sum of independent contributions of rotational and vibrational degrees of freedom. The latter model predicts at low temperatures the ratio of bulk and shear viscosity coefficients in CO_2 up to several thousands. It is shown that applying the consistent theoretical approach does not allow splitting the bulk viscosity to the rotational and vibrational contributions. The maximum ratio ζ/η obtained while using the accurate model is about 5 at $T = 2000$ K; the contribution of vibrational degrees of freedom (which are practically frozen under low-temperature conditions) is found to be significantly lower compared to that of rotational modes.

Another important result of this work is the general algorithm developed for the calculation of vibrational relaxation time taking into account excitation of all CO_2 vibrational modes and multiple channels of vibrational relaxation. First calculations showed a non-monotonic temperature dependence of the relaxation time, similar to that discussed recently for diatomic species. For preliminary estimates, some simplifying assumptions are introduced and only a few lowest states are taken into account. In the future work we plan to include all vibrational states and possible vibrational energy transitions to the calculations.

ACKNOWLEDGMENTS

This study is supported by the Russian Foundation for Basic Research grant 18-31-00110.

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