Ab initio CALCULATION OF TRANSPORT PROPERTIES OF SUPERCRITICAL CARBON DIOXIDE

Gerold STEINEBRUNNER[1], Anthony J. DYSON[2], Barbara KIRCHNER[3]
and Hanspeter HUBER[4,]*

Institut fur Physikalische Chemie, Universitat Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland; e-mail: [1] gerold.steinebrunner@elca.ch, [2] tdyson@ozemail.com.au, [3] kirchner@ubaclu.unibas.ch, [4] huber@ubaclu.unibas.ch

Received April 8, 1998
Accepted June 11, 1998

Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.

Self diffusion, shear viscosity and thermal conductivity of carbon dioxide are determined fully *ab initio* using two different intermolecular potential energy surfaces. These properties are calculated using the time-correlation formalism in classical equilibrium molecular dynamics simulations. The self diffusion constant is in addition determined from the Einstein relation. For the shear viscosity we use two different models of momentum localization: at the center of mass of the molecules, or at each atom. For the thermal conductivity we apply the formulae for rigid and flexible molecules assuming energy localization at the center of mass of the molecules. The results obtained are in good agreement with experiment. A fully *ab initio* calculation of transport properties allows for a prediction of these quantities even at state points where experiments are hardly possible.

Key words: Carbon dioxide; Transport properties; *Ab initio* calculations; Self diffusion; Shear viscosity; Thermal conductivity; Supercritical state.

In recent years, carbon dioxide has gained importance as a solvent for organic substances (see for example refs[1–5]). The physical properties of fluid carbon dioxide are of crucial interest for many industrial processes. For example, where chemical reactions are performed in a large vessel, accurate knowledge of the thermal conductivity is of great importance. In this article we report calculations of the transport properties of fluid CO_2, carried out from pure theory. Such calculations permit the accurate estimation of these quantities over a wide range of phase points, including regions in which experimental determination is impractical.

---

* The author to whom correspondence should be addressed.

COMPUTATIONAL DETAILS

Molecular dynamics simulations of CO_2 in the supercritical state were performed, applying two *ab initio* pair potentials calculated previously in our group[6,7]. These potentials were calculated using a (11s6p2d)/[5s4p2d] and (13s8p4d1f)/[8s6p4d1f] basis, respectively, including electron correlation by second order Møller–Plesset perturbation theory. In the construction of the two potentials, the interactions were separated into two parts: an intermolecular pair potential, and an intramolecular potential. The intermolecular contribution was determined using pairs of molecules fixed in their equilibrium configurations, calculating the dimer interaction energy at the level of theory described above. The intramolecular contribution was then approximated using a harmonic potential, calibrated to the vibrational frequencies of an isolated molecule. These frequencies were again determined using quantum chemical calculations at the same level of theory. For a full description we refer the reader to refs[6,7].

For the molecular dynamics simulations, 216 flexible molecules were placed in a cubic box, and periodic boundary conditions were applied. The equations of motion were solved using the leap-frog version of the Verlet algorithm[8]. In order to save computer time a multiple time step procedure[8] was applied. Whereas the intramolecular forces were calculated at each time step, the intermolecular forces were evaluated only every third step, and in between were approximated using a second order Taylor expansion.

The transport properties were determined using the time-correlation formalism. In general, a transport quantity K is described by[9]

$$K = C_K \int_0^\infty \mathrm{d}t \, \langle \dot{A}_K(t) \dot{A}_K(0) \rangle \;, \qquad (1)$$

where C_K is a specific constant for each transport quantity and $\dot{A}_K$ is the corresponding current (see below). For the shear viscosity and thermal conductivity three different models can be applied. Despite the fact that we deal with flexible molecules, the formulae for rigid molecules[10] can be applied while considering only the translation and rotation of a molecule. Alternatively, expressions for flexible molecules can be derived assuming the total energy and momentum to be localized at the center of mass of each molecule, or at every atom. These three models will in the following be called rigid, molecular and atomic model, respectively. In the case of the shear viscosity the rigid model and the molecular model are identical. For the thermal conductivity the three expressions are different, but the statistical error of the atomic model is of the same size as the result itself. Therefore, we give the thermal conductivity only for the rigid and the molecular model.

The simulations were performed with a time step of 0.25 fs and over a total time of 45 ps. To generate a reasonable statistical sample the simulations were run seven times with changed numerics, *i.e.* altogether over a total of 315 ps. In order to evaluate the transport properties in the simulation the autocorrelation functions were recorded every 3 fs. To obtain good convergence of the integrals the functions had to be determined over a time interval of 1.8 ps for the diffusion and the thermal conductivity, and 1.2 ps for the shear viscosity. A new function can already be recorded after the previous function has decayed by a factor of 1/*e*, *i.e.* after 0.225 ps in the case of diffusion, after 0.120 ps for the thermal conductivity, and after 0.075 ps for the shear viscosity. This yielded per batch a total of 200 functions for the diffusion, 375 for the thermal conductivity, and 600 for the shear viscosity, respectively.

Although the approximation of the total potential energy as a sum over pair interactions is widely employed, the neglect of many-body interactions is sometimes thought to be the source of certain deviations between calculated and measured values. In the fluid state, and when the interactions are weak, our experience has shown that a high quality pair potential can already produce results consistent with experiment, indicating that contributions to the transport properties due to many-body effects are quite small in these systems. For example, transport properties of argon[11] and neon[12], determined using molecular dynamics simulations with *ab initio* pair potentials, were found without exception to agree with experiment within the statistical errors of 5–10%. A study of fluid argon by Lee and Cummings[13], in which the effect of three-body forces on the viscosity was investigated, showed that including the three-body interactions decreased the values by about 3%. Although these findings are not directly transferable to the case of CO_2, they do give an indication that any deviation due to the neglect of many-body effects is unlikely to be significant in this study, given the quite large statistical uncertainty.

RESULTS AND DISCUSSION

Table I gives the results for all calculated transport properties at a temperature T = 321.3 K and a density ρ = 18 249 mol m^{-3}, Table II those at temperature T = 302.9 K and density ρ = 23 389 mol m^{-3}, and Table III those at temperature T = 300.6 K and density ρ = 18 249 mol m^{-3}. These points were chosen because experimental results were available for all three properties. The experimental values for the self diffusion constant in Table I and Table III were interpolated from ref.[14], whereas the one in Table II had to be extrapolated. The errors given for the experimental values for the self diffusion are estimated from the interpolation and extrapolation procedure. The experimental values for the shear viscosity and the thermal conductivity are taken from ref.[15]. Note that the self diffusion coefficients were measured using $^{13}CO_2$ whereas, for consistency with all of the other experimental data, our simulations were performed with $^{12}CO_2$. This could cause a deviation of up to two percent between our simulated self diffusion coefficients and the experimentally obtained values reported in ref.[14].

Diffusion

The diffusion describes the transport of particles. The corresponding current is therefore the velocity of the center of mass of the molecule. The diffusion constant D is given by an integral over time[16]

$$D = \frac{1}{3} \int_0^\infty \mathrm{d}t \, \langle \boldsymbol{V}_i(t) \boldsymbol{V}_i(0) \rangle \quad , \tag{2}$$

TABLE I
Simulated and experimental transport properties at density ρ = 18 249 mol m^{-3} using the two *ab initio* potentials

Property	Equation	[5s4p2d]	[8s6p4d1f]	Experimental
T_{sim}, K		320.9 ± 1.1	321.6 ± 1.2	321.3
D, 10^{-6} cm^2 s^{-1}	correlation (Eq. (*2*))	165 ± 1	176 ± 1	209 ± 2
	Einstein (Eq. (*3*))	174 ± 2	184 ± 3	
λ, 10^{-3} J m^{-1} s^{-1} K^{-1}	flexible (Eq. (*8*))	89 ± 17	89 ± 10	89
	rigid (ref.[10])	86 ± 3	87 ± 4	
η, 10^{-6} Pa s^{-1}	molecular (Eq. (*12*))	87 ± 5	73 ± 3	71
	atomic (Eq. (*13*))	96 ± 6	86 ± 6	

TABLE II
Simulated and experimental transport properties at density ρ = 23 389 mol m^{-3} using the two *ab initio* potentials

Property	Equation	[5s4p2d]	[8s6p4d1f]	Experimental
T_{sim}, K		302.5 ± 2.6	303.3 ± 1.1	302.9
D, 10^{-6} cm^2 s^{-1}	correlation (Eq. (*2*))	92 ± 3	96 ± 1	108 ± 6
	Einstein (Eq. (*3*))	97 ± 2	94 ± 3	
λ, 10^{-3} J m^{-1} s^{-1} K^{-1}	flexible (Eq. (*8*))	189 ± 20	137 ± 19	136
	rigid (ref.[10])	149 ± 11	151 ± 11	
η, 10^{-6} Pa s^{-1}	molecular (Eq. (*12*))	151 ± 8	145 ± 9	130
	atomic (Eq. (*13*))	128 ± 6	148 ± 6	

with $\boldsymbol{V}_i$ the center of mass velocity of molecule i, and $\langle \ldots \rangle$ indicates the average over all molecules and all correlation functions recorded during the simulation. Alternatively, the diffusion constant can be determined from the Einstein relation

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle |\boldsymbol{R}_i(t) - \boldsymbol{R}_i(0)|^2 \rangle \ , \tag{3}$$

where $\boldsymbol{R}_i$ is the center of mass coordinate of molecule i. In contrast to Eq. (*2*), the average $\langle \ldots \rangle$ is here only over all molecules.

Compared to experiment, the simulated results are roughly 15% too small. There seems to be a slight improvement going from the [5s4p2d] to the [8s6p4d1f] potential. In general, the Einstein relation yields results closer to the experiment although the statistical error of these results is slightly larger than that of those obtained from Eq. (*2*). We do not have any explanation for this behaviour. Results with similar deviations from experiment were obtained by Tsuzuki *et al.*[17]. They performed simulations with rigid molecules using an *ab initio* potential energy surface calculated in their group[18]. Somewhat larger is the deviation obtained in earlier work by Böhm *et al.*[19].

Thermal Conductivity

The thermal conductivity describes the transport of energy in a system. It is convenient to define the quantity

$$\boldsymbol{A}_\lambda = \sum_{i=1}^{N_{\text{mol}}} \boldsymbol{R}_i E_i \ , \tag{4}$$

TABLE III
Simulated and experimental transport properties at density ρ = 18 249 mol m^{-3} using the two *ab initio* potentials

Property	Equation	[5s4p2d]	[8s6p4d1f]	Experimental
T_{sim}, K		299.5 ± 1.1	301.6 ± 1.0	300.6
D, 10^{-6} cm^2 s^{-1}	correlation (Eq. (*2*))	158 ± 2	163 ± 2	184 ± 5
	Einstein (Eq. (*3*))	162 ± 2	168 ± 3	
λ, 10^{-3} J m^{-1} s^{-1} K^{-1}	flexible (Eq. (*8*))	95 ± 17	93 ± 12	89
	rigid (ref.[10])	84 ± 5	78 ± 3	
η, 10^{-6} Pa s^{-1}	molecular (Eq. (*12*))	70 ± 5	84 ± 5	71
	atomic (Eq. (*13*))	84 ± 4	108 ± 8	

with $\boldsymbol{R}_i$ the center of mass coordinate and E_i the total energy of molecule i (see below). The sum runs over all N_{mol} molecules. The corresponding current is the heat flux vector

$$\boldsymbol{j} = \frac{1}{V} \sum_{i=1}^{N_{\mathrm{mol}}} (\dot{\boldsymbol{R}}_i E_i - \boldsymbol{R}_i \dot{E}_i) \ , \tag{5}$$

where V denotes the volume of the system. The thermal conductivity λ is given by[8]

$$\lambda = \frac{V}{k_{\mathrm{B}} T^2} \int_0^{\infty} \mathrm{d}t \, \langle \boldsymbol{j}(t) \cdot \boldsymbol{j}(0) \rangle \tag{6}$$

with k_{B} Boltzmann constant and T the temperature. We assume the total energy E_i of a molecule to be located in its center of mass $\boldsymbol{R}_i$. The energy of a molecule consists of the kinetic energy of each single atom, the potential energy of the intramolecular vibrations V^{intra}, and its share of the intermolecular potential energy $V_{i\alpha}^{\mathrm{inter}}$. It is common to share the potential energy equally between interacting atoms[9]. The total energy reads[20]

$$E_i = \sum_{\alpha=1}^{n_{\mathrm{at}}} \frac{1}{2} m_{i\alpha} \boldsymbol{v}_{i\alpha}^2 + V^{\mathrm{intra}}(\boldsymbol{r}_{i1}, \boldsymbol{r}_{i2}, \boldsymbol{r}_{i3}) + \sum_{\alpha=1}^{n_{\mathrm{site}}} V_{i\alpha}^{\mathrm{inter}} \ . \tag{7}$$

Note that the sum of the kinetic energy (with the greek index) runs over the number of atoms per molecule n_{at} (*i.e.* 3 in the case of carbon dioxide), whereas the sum forming the intermolecular contribution runs over the number of intermolecular interaction sites per molecule n_{site} (*i.e.* 5 in the case of the two applied intermolecular interaction models for carbon dioxide[6,7]). Taking into account the pair additivity of the intermolecular potential the heat current then reads

$$\boldsymbol{j} = \frac{1}{V} \sum_{i=1}^{N_{\mathrm{mol}}} \boldsymbol{V}_i E_i + \frac{1}{V} \sum_{\substack{i,j=1 \\ i<>j}}^{N_{\mathrm{mol}}} \sum_{\alpha,\beta=1}^{n_{\mathrm{site}}} \frac{1}{2} \boldsymbol{R}_{ij} (\boldsymbol{F}_{i\alpha j\beta}^{\mathrm{inter}} \cdot \boldsymbol{v}_{i\alpha}) \ , \tag{8}$$

where $\boldsymbol{F}_{i\alpha j\beta}^{\mathrm{inter}}$ is the force of atom i in molecule α on atom j in molecule β. This model for the thermal conductivity yields large statistical errors. Alternatively, the formula for rigid molecules[10] can be applied.

The agreement with experiment is very good with the exception of the result for the flexible model obtained by the [5s4p2d] potential at 300 K and ρ = 23 389 mol m^{-3}. However, the flexible model always shows huge statistical errors due to the strong energy oscillations accompanying the vibrations. Hence, conclusions are difficult to draw. Wang *et al.*[21] emphasize that at the critical point the contribution of the intermolecular potential becomes very important. Their results were obtained from nonequilibrium molecular dynamics simulations, using an empirical Lennard–Jones potential and rigid molecules. The accuracy of their results is comparable to ours.

Figure 1 gives the time correlation functions of the heat flux vector for both models. The flexible model shows the expected oscillations, being probably the origin of the large statistical error. The dominating oscillation corresponds to the bending vibration. As discussed in previous work[7] the energy transfer between the vibrational and the other (rotational and translational) degrees of freedom takes place on a time scale of nanoseconds, whereas our simulations run only over 45 ps. This could mean that some slow fluctuations corrupt the results in the flexible model.

Shear Viscosity

The shear viscosity describes the transport of momentum in a system. In order to describe the shear viscosity η it is helpful to define the quantity

$$\boldsymbol{A}_\eta = \sum_{i=1}^{N_\mathrm{mol}} \boldsymbol{R}_i \otimes \boldsymbol{P}_i \ , \tag{9}$$

with $\boldsymbol{R}_i$ the center of mass coordinate and $\boldsymbol{P}_i$ the total momentum of molecule i. The ⊗ denotes the tensor product. The corresponding current is the pressure tensor

$$\sigma = -\frac{1}{V} \dot{\boldsymbol{A}}_\eta \ , \tag{10}$$

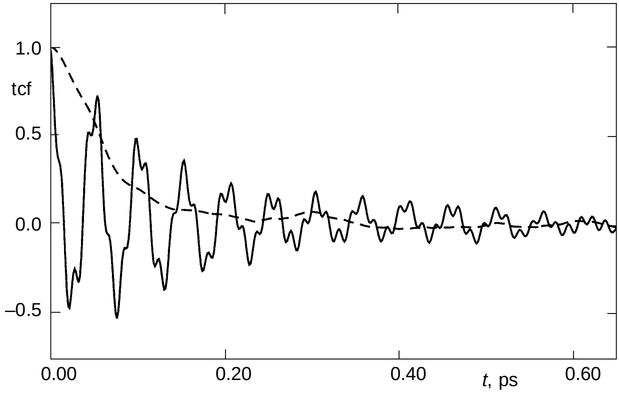

FIG. 1
Normalized time correlation functions (tcf) of the heat flux vector for the flexible and the rigid model at T = 300 K and density ρ = 23 389 mol m^{-3}; flexible model (full line), rigid model (dashed line)

where V is the volume. The viscosity reads[8]

$$\eta = \frac{V}{k_B T} \int_0^{\infty} \mathrm{d}t \, \langle \sigma^{xy}(t) \sigma^{xy}(0) \rangle \ , \tag{11}$$

where xy indicates the sum over the non-diagonal elements of the pressure tensor. As mentioned above, two different general assumptions can be made. On one hand, the total momentum $\boldsymbol{P}_i$ of a molecule can be considered to be located at the center of mass $\boldsymbol{R}_i$ of the corresponding molecule. This yields a final expression for the pressure tensor[22]

$$\sigma = -\frac{1}{V} \left(\sum_{i=1}^{N_{\mathrm{mol}}} M_i \boldsymbol{V}_i \otimes \boldsymbol{V}_i + \sum_{\substack{i,j=1 \\ j<>i}}^{N_{\mathrm{mol}}} \sum_{\alpha,\beta=1}^{n_{\mathrm{site}}} \boldsymbol{R}_{ij} \otimes \boldsymbol{F}_{i\alpha j\beta}^{\mathrm{inter}} \right) . \tag{12}$$

On the other hand, one can assume that the momentum $\boldsymbol{p}_{i,\alpha}$ of each atom is localized at the coordinate $\boldsymbol{r}_{i,\alpha}$ of each atom itself. Hence, the pressure tensor reads[22]

$$\sigma = -\frac{1}{V} \left(\sum_{i=1}^{N_{\mathrm{mol}}} \sum_{\alpha=1}^{n_{\mathrm{at}}} m_{i\alpha} \boldsymbol{v}_{i\alpha} \otimes \boldsymbol{v}_{i\alpha} + \sum_{i=1}^{N_{\mathrm{mol}}} \sum_{\alpha=1}^{n_{\mathrm{at}}} \boldsymbol{r}_{i\alpha} \otimes \boldsymbol{F}_{i\alpha}^{\mathrm{intra}} + \sum_{\substack{i,j=1 \\ j<>i}}^{N_{\mathrm{mol}}} \sum_{\alpha,\beta=1}^{n_{\mathrm{site}}} \frac{1}{2} \boldsymbol{r}_{i\alpha j\beta} \otimes \boldsymbol{F}_{i\alpha j\beta}^{\mathrm{inter}} \right) . \tag{13}$$

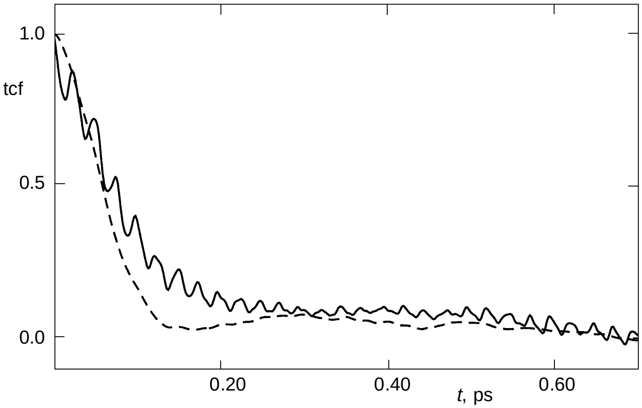

FIG. 2
Normalized time correlation functions (tcf) of the pressure tensor for the atomic and the molecular model at T = 300 K and density ρ = 23 389 mol m^{-3}; atomic model (full line), molecular model (dashed line)

The results of the simulation show no conclusive pattern. They are in general slightly larger than the experimental values, but the deviations are roughly within the statistical errors. Maréchal and Ryckaert[9] showed that the atomic and the molecular model lead to different autocorrelation functions but yield the same value for the shear viscosity. This is confirmed by our results. Figure 2 shows the difference in the time correlation functions. The atomic model shows an oscillation with exactly the frequency of the symmetric vibration of the carbon dioxide monomer. It can be shown from Eq. (*13*) that in the second sum, taking into account the intramolecular forces, the bending and the asymmetric stretching vibration do not contribute. Similarly, as for the conductivity, the long-time fluctuations of the vibrations could influence the results in the atomic model.

CONCLUSIONS

In this paper we have successfully applied two *ab initio* potentials to molecular dynamics simulations in order to calculate transport properties of carbon dioxide in the supercritical state from pure theory. The results show fair agreement with experiment. The self diffusion is in general too small but reproduces the correct temperature and density dependence. The thermal conductivity and the shear viscosity agree in general with the experimental values within the quite large statistical errors. The accuracy of these quantities allows for a prediction where experiments are not available. To improve the results the statistical errors should be reduced, which means still longer runs with more molecules.

REFERENCES

1. Rice J. K., Niemeyer E. D., Dunbar R. A., Bright F. V.: *J. Am. Chem. Soc*. **1995**, *117*, 5832.
2. Curren M. S., Burk R. C.: *J. Chem. Eng. Data* **1997**, *42*, 727.
3. Shen J. W., Kitao O., Nakanishi K.: *Fluid Phase Equilib.* **1996**, *120*, 81.
4. Clarke M. J., Harrison K. L., Johnston K. P., Howdle S. M.: *J. Am. Chem. Soc*. **1997**, *119*, 6399.
5. Kaupp G.: *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 1452.
6. Welker M., Steinebrunner G., Solca J., Huber H.: *Chem. Phys*. **1996**, *213*, 253.
7. Steinebrunner G., Dyson A. J., Kirchner B., Huber H.: *J. Chem. Phys*., in press.
8. Allen M. P., Tildesley D. J.: *Computer Simulations of Liquids.* Clarendon Press, Oxford 1987.
9. Marechal G., Ryckaert J.: *Chem. Phys. Lett.* **1983**, *101*, 548.
10. Hoheisel C.: *Phys. Rep*. **1994**, *245*, 111.
11. Ermakova E., Solca J., Huber H., Welker M.: *J. Chem. Phys*. **1995**, *102*, 4942.
12. Eggenberger R., Huber H., Welker M.: *Chem. Phys*. **1994**, *187*, 317.
13. Lee S. H., Cummings T.: *J. Chem. Phys*. **1994**, *101*, 6206.
14. Etesse P., Zega J. A., Kobayashi R.: *J. Chem. Phys*. **1992**, *97*, 2022.
15. Vesovic V., Wakeham W. A., Olchowy G. A., Sengers J. V., Watson J. T. R., Millat J.: *J. Phys. Chem. Ref. Data* **1990**, *19*, 763.
16. McQuarrie D.: *Statistical Mechanics*. Harper and Row, New York 1976.
17. Tsuzuki S., Uchimaru T., Mikami M., Tanabe K., Sako T., Kuwajima S.: *Chem. Phys. Lett.* **1996**, *255*, 347.

18. Tsuzuki S., Uchimaru T., Tanabe K., Kuwajima S., Tajima N., Hirano T.: *J. Chem. Phys*. **1996**, *100*, 4400.
19. Bohm H., Meissner C., Ahlrichs R.: *Mol. Phys*. **1984**, *53*, 651.
20. Daivis P. J., Evans D. J.: *Mol. Phys*. **1994**, *81*, 1289.
21. Wang B. Y., Cummings P. T., Evans D. J.: *Mol. Phys*. **1992**, *75*, 1345.
22. Cui S. T., Cummings P. T., Cochran H. D.: *J. Chem. Phys*. **1996**, *104*, 255.