International Journal of Thermophysics, Vol. 10, No. 1, 1989

Transport Coefficients of Liquid CF_4 and SF_6 Computed by Molecular Dynamics Using Polycenter Lennard–Jones Potentials[1]

C. Hoheisel[2]

For several liquid states of CF_4 and SF_6, the shear and the bulk viscosity as well as the thermal conductivity were determined by equilibrium molecular dynamics (MD) calculations. Lennard–Jones four- and six-center pair potentials were applied, and the method of constraints was chosen for the MD. The computed Green–Kubo integrands show a steep time decay, and no particular long-time behavior occurs. The molecule number dependence of the results is found to be small, and 3×10^5 integration steps allow an accuracy of about 10% for the shear viscosity and the thermal conductivity coefficient. Comparison with experimental data shows a fair agreement for CF_4, while for SF_6 the transport coefficients fall below the experimental ones by about 30%.

KEY WORDS: CF_4; Lennard–Jones fluid; molecular dynamics calculations; SF_6; transport coefficients.

1. INTRODUCTON

For liquids composed of spherically symmetric particles, transport coefficients such as the shear viscosity, η_s, the bulk viscosity, η_v, and the thermal conductivity, λ, can be computed with an accuracy of about 5% by equilibrium and nonequilibrium molecular dynamics (MD) methods [1–3]. In contrast, the investigation of transport coefficients of systems containing molecules by MD is, at present, still in a preliminary stage.

The shear viscosity of liquid butane determined by two different MD

---

[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstr. 150, 4630 Bochum, Federal Republic of Germany.

methods differs, for example, by a factor of about 2 [4–5]. Thus we have chosen here simply structured molecules for our study to perform sufficiently long MD runs allowing an accurate determination of the autocorrelation functions (ACFs). Moreover, comparison with experimental data is made ensuring that the Lennard–Jones (LJ) potentials employed are fairly adequate.

Table I. Technical Details of the MD Calculations

(A) General remarks	
Molecule number N	32, 108
Ensemble	$NVE\mathbf{p}$: V, volume; E, total energy; $\mathbf{p}$, total momentum
Integration algorithm	Stoermer–Verlet
Integration time step	0.5×10^{-14} s
Starting configuration	Liquid like
Equilibration time	1000–2000 steps
(B) Computations with the 6-center LJ potential	
Production runs	10^5 steps ($N = 32$) 0.65×10^5 steps ($N = 108$)
Averaging events for correlation functions	5000–10,000 ($N = 32$) 3000–6000 ($N = 108$)
Computation time for 10^3 steps (Cyber 205)	30.8 s ($N = 32$) 172.5 s ($N = 108$)
Cutoff radius for the LJ potential	2.55σ ($N = 32$) 3.50σ ($N = 108$)
(C) Computations with the 4-center LJ potential	
Production runs	2×10^5 steps ($N = 32$) 1.2×10^5 steps ($N = 108$)
Averaging events for correlation functions	7500–15,000 ($N = 32$) 5000–10,000 ($N = 108$)
Computation time for 10^3 steps (Cyber 205)	16.4 s ($N = 32$) 91.7 s ($N = 108$)
Cutoff radius for the LJ potential	2.23σ ($N = 32$) 3.20σ ($N = 108$)
(D) Computations with the 1-center LJ potential	
Production runs	0.85×10^5 steps ($N = 108$)
Averaging events for correlation functions	3500–5000
Computation time for 10^3 steps (Cyber 205)	11.6 s ($N = 108$)
Cutoff radius for the LJ potential	2.5σ

Table II. Lennard-Jones Potential Parameters and Characteristic Separations of the Interaction Centers for Model SF_6 and CF_4

(A) 6-center interaction potential with the sites in rhombic configuration	
LJ parameters	$\sigma = 2.70$ Å, $\varepsilon k_B^{-1} = 60.0$ K
Atomic-site center of mass[a] separation[b]	1.561 Å
(B) 4-center interaction potential with the sites in tetrahedral configuration	
LJ parameters	$\sigma = 2.71$ Å, $\varepsilon k_B^{-1} = 87.5$ K
Atomic-site center of mass[c] separation[d]	1.54 Å
(C) 1-center interaction potential for the representation of the CF_4–CF_4 interaction	
LJ parameters	$\sigma = 4.15$ Å, $\varepsilon k_B^{-1} = 175$ K

[a] Mass of the molecule, 146.04 AU.
[b] Experimental S–F bond length, 1.561 Å.
[c] Mass of the molecule, 88.0 AU.
[d] Experimental C–F bond length, 1.322 Å.

2. MD COMPUTATIONS, POTENTIALS, AND THERMODYNAMIC STATES

The MD computations for the molecular systems have been performed using the "contraints method" introduced by Ciccotti and co-workers [4, 6]. We used a fully vectorized program version described in detail in Refs. 7 and 8. The technical data of the present MD runs are summarized

Table III. Comparison of Measured and Calculated Pressures of SF_6[a]

T (K)	ρ ($g \cdot cm^{-3}$)	p^{MD} (bar)	p^{EXP} (bar)
325	1.400	140	120
240	1.826	320	120
250	1.900	500	410

[a] Experimental data from Ref. 10. Statistical error of the MD values, 20–30%.

Table IV. Thermodynamic States of SF_6 Considered for the Computations

State point	T (K)	ρ $(g \cdot cm^{-3})$
1	250	1.5
2	250	1.6
3	250	1.7
4	250	1.8
5	250	1.9
6	223	1.848 (triple point)
7	220	1.980

in Tables IA–IC. For comparison, we performed additional MD calculations with structureless particles by modeling CF_4 with an one-center Lennard–Jones potential [7]. The details of these computations are given in Table ID.

The polycenter LJ potentials used for SF_6 and CF_4 are characterized by the configuration of the interaction centers and the two potential parameters ε and σ. For SF_6 we employed six centers ordered in a rhombic form, and for CF_4 four centers in a tetrahedral structure. The significant separations between the centers as well as the LJ potential parameters are given in Tables IIA and IIB. Table IIC contains the one-center LJ potential parameters for the alternative description of the CF_4 interaction.

The LJ potential parameters have been adopted from Refs. 7 and 9. For SF_6, a few test runs were necessary to readjust the potential parameters in order to obtain the pressure of the system in agreement with experiment.

We show some MD pressure values in comparison with measured data of SF_6 [10] in Table III. The statistical uncertainty for the theoretical results is rather large, as we performed only small runs with 108 particles.

For CF_4, we inserted straightforwardly the LJ potential parameters optimized in Ref. 7 but introduced a slight reduction of the σ parameter to avoid equilibration difficulties for the state of 120 K.

We considered typical liquid states at saturation conditions or fluid states at elevated pressures up to 500 bar. The state points are listed in Table IV as far as SF_6 is concerned. For CF_4 we chose exactly the same states as given in Ref. 7.

3. FORMULATION OF THE MICROSCOPIC CURRENTS IN "MOLECULE VARIABLES"

Following Marechal et al. [4], we may express the microscopic viscous flow $\underline{J}_p$ of a system of N molecules, each molecule consisting of n atomic centers, by

$$\underline{J}_p = M \sum_{\alpha=1}^{N} \dot{\underline{R}}_\alpha \dot{\underline{R}}_\alpha - \frac{1}{2} \sum_{\alpha \neq \beta}^{N}\sum \sum_{i,j}^{n}\sum \underline{R}_{\alpha\beta} \cdot \nabla\phi(r^{ij}_{\alpha\beta}) \tag{1}$$

where i, j denote atomic sites and α, β molecules, $\underline{R}$ refers to molecules and $\underline{r}$ to atom centers, ϕ denotes the pair interaction potential between the atomic interaction centers of different molecules, and M denotes the mass of a molecule. The notations $\underline{R}_\alpha$, $\underline{R}_{\alpha\beta}$, and $r^{ij}_{\alpha\beta}$ indicate explicitly the position vector of the center of mass of molecule α, the difference of two center of mass position vectors of molecules α and β, and the separation of two atomic centers i, j of two molecules α, β, respectively.

Accordingly, the heat current $\underline{J}_q$ may be expressed in molecule quantities as follows:

$$\underline{J}_q = \frac{M}{2} \sum_{\alpha=1}^{N} \dot{\underline{R}}_\alpha^2 \dot{\underline{R}}_\alpha - \frac{1}{2} \sum_{\alpha=1}^{N} \sum_{i=1}^{n} \dot{\underline{r}}^i_\alpha \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^{N} \sum_{j=1}^{n} [\underline{R}_{\alpha\beta} \nabla\phi(r^{ij}_{\alpha\beta}) - \phi(r^{ij}_{\alpha\beta})\mathbf{i}] \tag{2}$$

where $\mathbf{i}$ denotes the unit tensor.

The desired transport coefficients are obtained using the Green–Kubo integrals over the correlation functions containing the fluxes, i.e., the sums over suitable elements of the tensors. For molecule systems the off-diagonal terms of the "potential parts" of the tensors occurring in the dynamic variables are generally not equal. So the transport coefficient is evaluated with the use of a symmetrized form of these tensor elements [4]. For the present case of very "symmetric" globular molecule models, the difference between these nondiagonal tensor elements is numerically completely negligible, as we ensured by several test computations.

4. SHEAR VISCOSITY, BULK VISCOSITY, AND THERMAL CONDUCTIVITY OF SF_6 AND CF_4

4.1. The Time Correlation Functions

The total time autocorrelation functions (ACFs) for the shear viscosity, η_s, the bulk viscosity η_v, and the thermal conductivity, λ, computed by MD are shown for state point 4 of SF_6 in Figs. 1–3. All three ACFs decay very quickly with time and vanish completely after about 1 ps.

We ensured this by parallel runs with 108 particles, where we computed the ACFs up to 3 ps. Excepting the ACF for η_v, which exhibits large fluctuations at longer times, the ACFs of the SF_6 model allow an accurate integration and thus reliable transport coefficients.

Similar encouraging results were found for the CF_4 model liquid. In Fig. 4 we display as an example the plot of the ACF for η_s at 140 K.

To study further the partial contributions to the total Green–Kubo integrands, we computed separately the kinetic–kinetic (kk), the potential–potential (pp), and the potential–kinetic (pk) terms of the total ACFs. These calculations showed that the kk term as well as the pk term is very small, contributing at most 5% to the total ACF. Figures 1–3 display, in addition to the total ACF, the pp part. We see that the total functions are practically represented by the pp part, which corroborates our above statement.

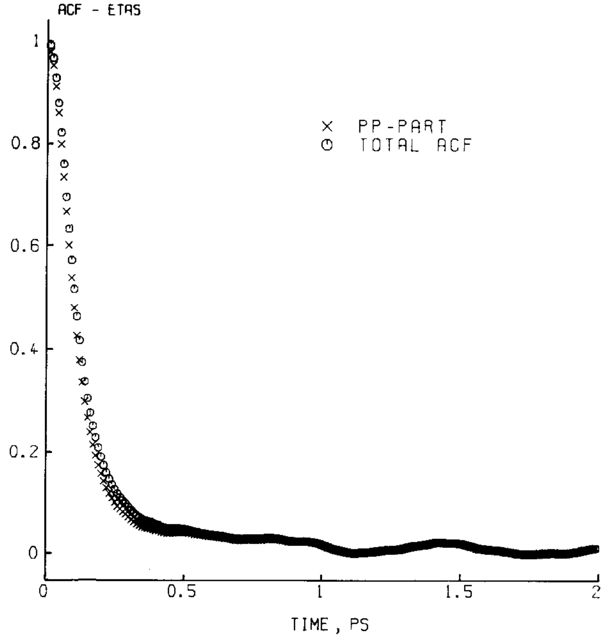

Fig. 1. Total autocorrelation function (ACF) and partial potential–potential (pp) contribution for the shear viscosity, η_s, of six-center Lennard–Jones (LJ) SF_6. The ACF and the partial ACF are normalized by the same factor. $N = 32$; state point 4.

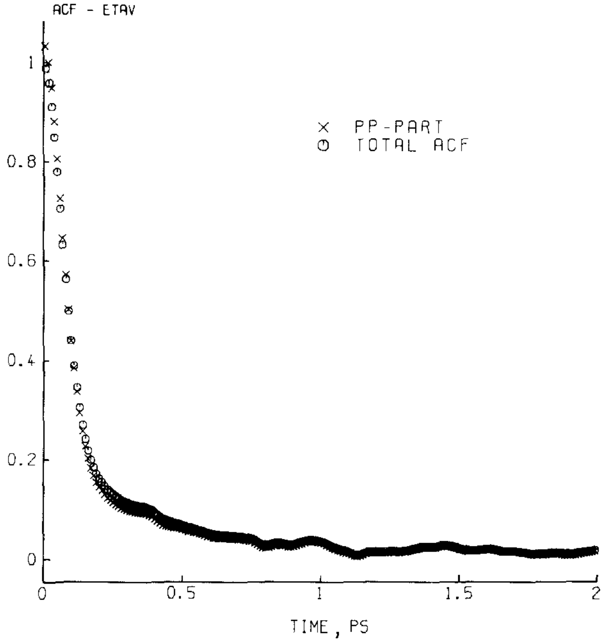

Fig. 2. As Fig. 1, but for the bulk viscosity, η_V.

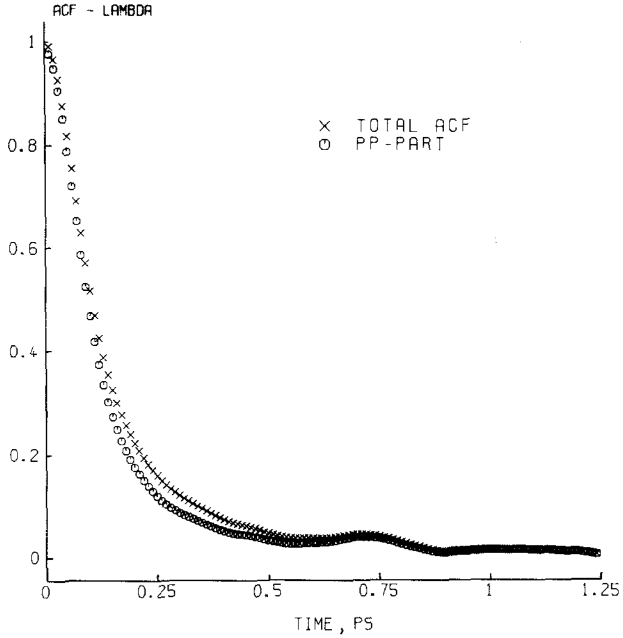

Fig. 3. As Fig. 1, but for the thermal conductivity, λ.

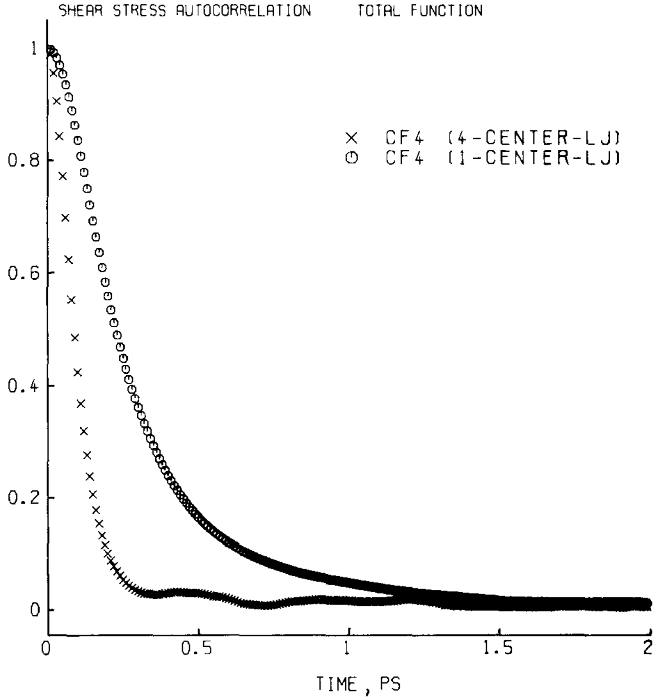

Fig. 4. Total ACFs for η_s of four-center and one-center LJ CF_4: 140 K; 1.632 $g \cdot cm^{-3}$.

4.2. Transport Coefficients for SF_6 and CF_4

For SF_6, there exist two experimental investigations of η_s and λ for various liquid and fluid states [10, 11]. We compare our MD results with the experimental ones in Table V. It is to be emphasized that the theoretical coefficients stem from an average over at least three different runs with 32 or 108 particles, while the ACFs shown in the figures are obtained from a single run each. By these different runs we determined an error bar of ±0.02–0.03 for the normalized ACFs. The scatter of the curves leads to an uncertainty of about 20% for the transport coefficients η_s and λ. Using three or four computations the error for the mean values can be estimated to about 10%. Table V shows that the MD values are generally lower than the experimental ones by about 30%. The bulk viscosity also listed in Table V cannot be compared with experimental data. These theoretical values have a much larger statistical error, as the uncertain plateau value of the integral over the correlation function indicated. From

Table V. Comparison of Transport Coefficients of Liquid SF_6 Computed by MD with a Six-Center Potential and Obtained by Experiment[a]

State point	$10^4\,\eta_s^{\mathrm{MD}}$ (Pa·s)	$10^4\,\eta_s^{\mathrm{EXP}}$ (Pa·s)	λ^{MD} ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	λ^{EXP}[b] ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	$10^4\,\eta_v^{\mathrm{MD}}$ (Pa·s)
1	1.20 ± 0.05	1.65	28 ± 2	49	1.8
2	1.40 ± 0.05	2.15	32 ± 2	55	2.5
3	1.75 ± 0.1	2.65	41 ± 3	65	2.6
4	2.25 ± 0.15	3.65	46 ± 3	75	2.7
5	3.00 ± 0.2	4.85	54 ± 3	86	3.3
	(3.05 ± 0.3)		(62 ± 6)		(2.1)
6	2.5 ± 0.3		50 ± 3		3.4
7	3.7 ± 0.4		58 ± 5		5.2
	(3.1 ± 0.6)		(67 ± 7)		(5.0)

[a] Experimental error for η_s, 2–5% [10]. MD values in parentheses computed with 108 molecules.

[b] From Ref. 11, extrapolated. Estimated uncertainty, 10%.

our present computations, we estimate the statistical accuracy for η_v to be about 50%.

For liquid CF_4, the theoretical and experimental transport coefficients are summarized in Table VI. The statistical accuracy of η_s and λ for CF_4 has been determined in the same way as described for SF_6. An average error of about 7% resulted for η_s and λ. For η_v we obtained an estimate of about 30%. Unfortunately, there exist only experimental values for η_s and λ [12, 13]. Agreement between these experimental numbers and our calculated coefficients is good.

We have tested the molecule number dependence of the transport coefficients computed for SF_6 and CF_4. By means of about 20 runs of various starting conditions and total integration times with 32 and 108 molecules, we found the following.

(i) The ACFs for η_s and λ of CF_4 show no significant dependence on the molecule number N for all the thermodynamic states considered.

(ii) The ACF for η_s of SF_6 is independent of N for all the states investigated.

(iii) The ACF for λ of SF_6 depends significantly on N for states 5–7. It gives a value larger by about 10% for computations with 108 molecules compared to those with 32 molecules.

Table VI. Comparison of Transport Coefficients of Liquid CF_4 Determined by MD[a] Based on a Four-Center Molecular and an One-Center Atomic Lennard–Jones Potential and Obtained Experimentally

ρ $(\mathrm{g \cdot cm^{-3}})$	T (K)	$10^4\,\eta_s^{\mathrm{MD\text{-}MOL}}$ $(\mathrm{Pa \cdot s})$	$10^4\,\eta_v^{\mathrm{MD\text{-}MOL}}$ $(\mathrm{Pa \cdot s})$	$\lambda^{\mathrm{MD\text{-}MOL}}$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	$10^4\,\eta_s^{\mathrm{MD\text{-}ATO}}$ $(\mathrm{Pa \cdot s})$	$10^4\,\eta_v^{\mathrm{MD\text{-}ATO}}$ $(\mathrm{Pa \cdot s})$	$\lambda^{\mathrm{MD\text{-}ATO}}$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
1.531	160	2.18	2.8 ± 0.9	93.5 78.4[b]	1.74	0.870 ± 0.05	53
1.632	140	3.20 3.00[c]	2.6 ± 0.9	109	2.23	0.991 ± 0.05	58
1.720	120	4.54	3.7 ± 0.9	129	2.88	1.105 ± 0.05	70

[a] The statistical error of the MD values amounts to 5% for the atomic system and 5–8% for the molecular system, if no other errors are given. Results obtained by computations with 32 and 108 molecules differed insignificantly.

[b] Experimental value for 173 K [13].

[c] Estimated experimental value for 146 K [12].

These findings are summarized in Table V, where the transport coefficients resulting from computations with different N are given.

We conclude that the molecule number dependence of transport coefficients of these molecular systems is evidently smaller than the particle number dependence of these quantities of atomic models like LJ argon at the triple point [3]. In a sense this is not so striking, as for instance, the 108-molecule system of LJ SF_6 contains 648 atoms.

5. DISCUSSION AND CONCLUSIONS

Our MD computations show that transport coefficients such as the shear viscosity can be reliably obtained for liquid systems containing globular model molecules. While our employed six-center LJ potential generates transport coefficients too low for liquid SF_6, the four-center LJ potential can successfully be used to calculate η_s and λ of liquid CF_4. Improvements of the six-center potential model for SF_6 are possible and may be the subject of further investigations.

The ACFs of the molecular system presented here agree roughly with those found for the atomic systems, as expected. However, a direct comparison is interesting. For this purpose, we computed the correlation functions for the one-center LJ CF_4 liquid (see table IIc). Although the one-center potential does not give transport coefficients in good agreement with those of the four-center LJ liquid, as Table VI indicates, it is satisfactory for such a comparison.

The ACFs for η_s of CF_4 computed with both the four-center LJ and the one-center LJ potential are illustrated in Fig. 4. Evidently, the ACF of the molecular system has a much more pronounced "chair" form than the ACF of the atomic liquid. This agrees with the recent results for liquid model butane obtained by the Belgian authors [4].

ACKNOWLEDGMENTS

I thank R. Vogelsang for discussions and plots and U. Krupinski for typing.

REFERENCES

1. W. G. Hoover, D. J. Evans, R. B. Hickmann, A. J. C. Ladd, W. T. Ashurst, and B. Moran, *Phys. Rev.* **A22**:1690 (1980).
2. C. Trozzi and G. Ciccotti, *Phys. Rev.* **A29**:916 (1984).
3. C. Hoheisel and R. Vogelsang, *Comp. Phys. Rep.* **8**:1 (1988).
4. G. Marechal, J.-P. Ryckaert, and A. Bellemans, *Mol. Phys.* **61**:33 (1987).
5. R. Edberg, G. P. Morriss, and D. J. Evans, *J. Chem. Phys.* **86**:4555 (1987).

6. G. Ciccotti and J. P. Ryckaert, *Comp. Phys. Rep.* **3**:345 (1986).
7. M. Schoen, C. Hoheisel, and O. Beyer, *Mol. Phys.* **58**:699 (1986).
8. C. Hoheisel, R. Vogelsang, and M. Schoen, *Comp. Phys. Commun.* **43**:217 (1987).
9. G. S. Pawley, *Mol. Phys.* **43**:1321 (1981).
10. S. A. Ulybin and I. R. Makrushkin, *Teplofiz. Vys. Temp.* **15**:1195 (1977) (translated by Plenum).
11. S. S. Bakulin and S. A. Ulybin, *Teplofiz. Vys. Temp.* **16**:59 (1978) (translated by Plenum).
12. J. J. van Loef, *Physica* **B103**:133 (1981).
13. D. T. Jamieson, J. B. Irving, and J. S. Tudhope, *Liquid Thermal Conductivity. A Data Survey to 1973* (Her Majesty's Stationary Office, Edinburgh, 1975).