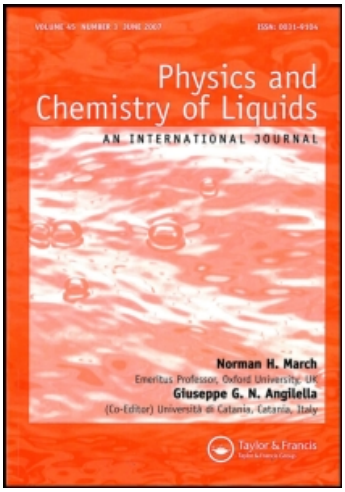

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Thermal Conductivity and Shear Viscosity of Liquid and Fluid Argon. An Extended Comparison between Experimental and Molecular Dynamics Data

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Thermal Conductivity and Shear Viscosity of Liquid and Fluid Argon. An Extended Comparison between Experimental and Molecular Dynamics Data

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We compare the thermal conductivity, λ, and the shear viscosity, η_s, of liquid and dense fluid argon obtained by experiment and computed by molecular dynamics (MD) using the Lennard-Jones pair potential. A wide region of states of reduced densities between 0.65 and 0.85 and temperatures of 0.7–3.5 is systematically investigated. For liquid states and dense fluid states up to reduced temperatures of about 2.5, agreement between experiment and theory is excellent. For states of higher temperatures and pressures, significant discrepancies appear for λ. However, for the latter states there exist no direct measurements of λ, and we are left with the fit equation given by Younglove and Hanley, which cannot reliably be used for pressures larger than 200 MPa, as these authors stated.

Key Words: Shear viscosity, thermal conductivity, Lennard-Jones potential, molecular dynamics.

1 INTRODUCTION

During the last five years the thermal conductivity, λ, and the shear viscosity, η_s, have accurately been determined by equilibrium molecular dynamics (MD) calculations and non-equilibrium MD techniques[1,2,3,4]. Frequently, the pseudo triple point of Lennard-Jones argon has been studied, and for this state, good agreement between calculation and experiment was found [2,3]. Some further thermodynamic states of argon were investigated [1,3,4], however a systematic comparison of MD and experimental data has not been attempted.

Such a comparison seemed to be of particular interest, as exceptionally the transport coefficients λ and η_s of argon are measured for a large region of dense states. Furthermore, there exist useful fit equations [5,6,7] for these measured transport coefficients which permit a reliable comparison with MD data.

We have therefore performed equilibrium MD calculations for Lennard-Jones Ar, and determined λ and η_s for many liquid and fluid states to compare in detail with experiment. Though we found good agreement in general, discrepancies occured for high pressure states.

2 THE MD CALCULATIONS

Our molecular dynamics calculations have been described previously [3,4]. We use the Störmer-Verlet integration algorithm and work in the conventional NEV **p** ensemble, where N denotes the particle number, E the total energy, V the volume and **p** the total momentum.

The Lennard-Jones (12-6) potential was employed for the pair interaction of particles, and the parameters were chosen to model dense argon. Useful technical details of the calculations may be found in Table 1.

Table 1

A. *MD calculations*	
Number of particles	108, 256, 500 (Standard: 256)
Number of integration steps for production runs	10^5
Integration time step	10^{-14}s
Potential cut off radius	2.5σ
CPU-time (in s) per 1000 integration steps (Cyber 205)	28.5 ($N = 256$)
B. *Lennard-Jones (12–6) potential parameters for argon*	
σ 3.405 Å	
ε/k 119.8 K	(k: Boltzmann constant)
C. *Units*	
Reduced density	$\frac{N}{V}\sigma^3 = n^*$
Reduced temperature	$T\frac{k}{\varepsilon} = T^*$
Reduced shear viscosity	$\eta_s \frac{\sigma^2}{(m\varepsilon)^{1/2}} = \eta_s^*$
Reduced thermal conductivity	$\lambda \frac{\sigma^2}{k}\left(\frac{m}{\varepsilon}\right)^{1/2} = \lambda^*$

The transport coefficients η_s and λ were obtained from the Green-Kubo integrals over the relevant time correlation functions. These formulae including the definitions of the shear viscous flow and the heat current are given in previous papers[2,3,4].

According to the large number of MD time steps carried out, the accuracy of the transport coefficients is of about 5 per cent for each of the thermodynamic states studied herein [3,4]. Moreover, extended MD runs exclude the occurrence of artificial metastabile states which may produce faulty transport coefficients.

3 EXPERIMENTAL VALUES FOR λ AND η_s

Hanley and coworkers have compiled reliable experimental data for the shear viscosity and the thermal conductivity of dense argon [5,7]. These authors gave useful fit equations for the coefficients in a range of states which has been investigated in the present work. Our comparison is based on these fits. The average error for these was estimated to be 2-4 per cent, which agrees very well with our own findings. Depending on density the general temperature range of the validity of the fit equations is:

$$0.9 \leq T^* \leq 2.5,$$

where T^* denotes the reduced temperature.

However, we indicate the precise limits in the figures where the data are displayed. As there are some minor misprints in the fit equations given by Younglove and Hanley [7], we repeat the corrected correlation equations in the Appendix.

4 RESULTS

4.1 Shear Viscosity

For three reduced densities, $n^* = 0.85, 0.75$ and 0.65, we have calculated η_s for reduced temperatures between 0.7 and 3.5. Table 2 contains these numbers together with the experimental values. We additionally show a few calculated pressures in the table to indicate the high pressure states. For illustration, we have plotted the MD results and the fitted experimental data in Figure 1. From this figure, we see the following

i) at all densities, there exists excellent agreement between the experimental and the MD results for the whole temperature range.

Table 2 Comparison of experimental shear viscosities* and MD results for liquid and fluid argon

n^*	T^*	$p^{(MD)}$/MPa**	$*^{(MD)}$ η_s	$*^{(EXP)}$ η_s
0.85	0.68		3.60	3.85
	0.75		3.33	3.08
	0.75		3.28	3.08
	0.91		3.09	2.77
	1.00		2.84	2.68
	1.03		2.75	2.65
	1.32	154	2.56	2.48
	1.50	191	2.44	2.42
	1.50		2.52	2.42
	1.98	287	2.28	2.32
	2.00		2.31	2.32
	2.53	380	2.29	2.27
	2.91	453	2.30	2.26
	3.02	457	2.30	2.25
	3.43	520	2.51	2.25
0.75	1.00		1.59	1.62
	1.01		1.66	1.62
	1.03		1.47	1.61
	1.33		1.68	1.53
	1.50	100	1.54	1.52
	2.02	176	1.51	1.51
	2.05		1.43	1.51
	2.50	230	1.53	1.52
	2.91	286	1.53	1.54
	3.00		1.48	1.54
	3.36	342	1.56	1.56
	3.46	353	1.49	1.56
0.65	1.59		0.89	1.00
	1.85		0.99	1.02
	2.53	147	1.02	1.06
	3.00	189	1.15	1.10
	3.56	238	1.01	1.13

* Reduced units are used (see Table 1).

** The statistical error for the pressure p is smaller than 5 per cent.

ii) the steep increase of η_s near the triple point of argon is well reflected by the model calculations.

Apparently, the Lennard-Jones potential is very well suited to represent the effective pair interaction in dense argon for calculation of experimental shear viscosities in a large thermodynamic range. Even in the neighbourhood of the phase transition to the solid state, the

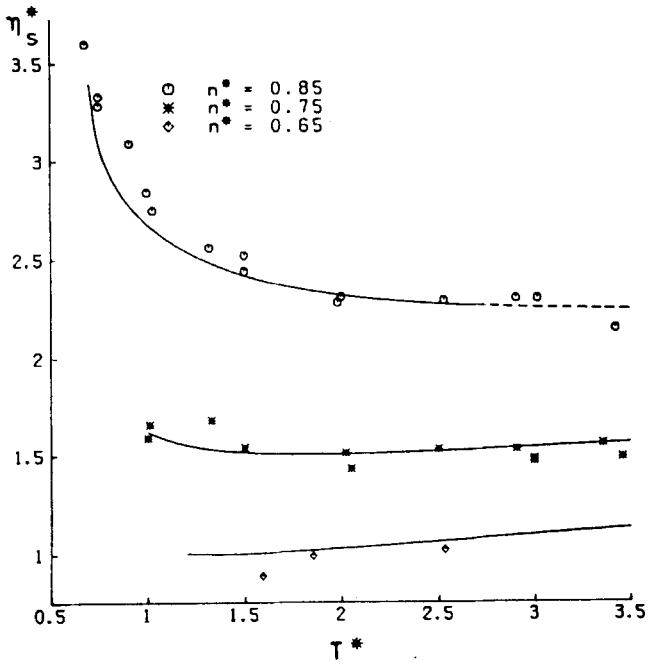

Figure 1 Experimental (full line) and MD (symbols) shear viscosities as a function of temperature at three densities. The dashed line indicates the invalidity of the fit for the experimental values.

behaviour of the experimental η_s-values is well predicted by the MD calculations based on this potential.

4.2 Thermal Conductivity

Table 3 contains the calculated and correlated experimental values of the thermal conductivity for similar states as studied in Section 4.1. The comparison is illustrated in Figure 2, where original MD data and experimental results represented by the fit of Younglove and Hanley have been plotted. Again very good agreement between MD and experimental results is found for the two lowest densities.

However, at $n^* = 0.85$ there occur significant discrepancies between the MD data and the fit for temperatures higher than about 2.0. For these states, the MD λ-values lie noticeably below the corresponding fit data. On the other hand, Younglove and Hanley stated two restrictions of their fit equation:

Table 3 Comparison of experimental thermal conductivities* and MD results for liquid and fluid argon

n^*	T^*	$p^{(MD)}$/MPa	$\lambda^{*(MD)}$	$\lambda^{*(EXP)}$	
0.85	0.73		7.16	7.13	
	0.80		7.10	6.97	
	0.90		7.25	6.99	
	0.92		7.18	7.02	
	1.00		7.34	7.16	
	1.02		7.34	7.20	
	1.27	154	7.23	7.83	
	1.54	193	7.34	8.50	
	1.76	246	8.12	8.98	
	1.98	287	8.08	9.39	(8.46)**
	2.00		8.08	9.42	(8.49)
	2.24	338	8.46	9.81	(8.87)
	2.53	380	8.78	10.22	(9.15)
	2.91	453	8.45	10.66	(9.53)
0.75	1.05		5.29	5.32	
	1.05		5.43	5.32	
	1.25		5.36	5.43	
	1.32		5.60	5.48	
	1.50	100	5.53	5.63	
	2.02	170	5.70	6.06	
	2.02		6.07	6.06	
	2.45	230	6.12	6.36	
	2.91	286	7.03	6.64	
	2.93		6.67	6.65	
	3.47	353	7.22	6.92	
0.65	1.25		3.89	4.02	
	1.48		4.18	4.11	
	1.59		4.14	4.16	
	1.96		4.46	4.33	
	2.53	147	4.79	4.59	
	2.53		4.79	4.59	
	3.00	189	5.02	4.77	
	3.56	238	5.30	4.97	

* Reduced units (see Table 1).
** Values in brackets correspond to $n^* = 0.83$.

i) the upper limit of the density is set to $n^* = 0.83$, for temperatures $T^* \leq 2.00$

ii) it cannot be used reliably for pressures greater than 200 MPa.

We have therefore additionally plotted the limiting curve, which corresponds to this pressure, in Figure 2. The plot indicates clearly that for densities of 0.85 the comparison is only permitted up to temperatures of about 1.5. We believe that for higher temperature the MD data give a more realistic tendency of λ than the extrapolated values of the fit

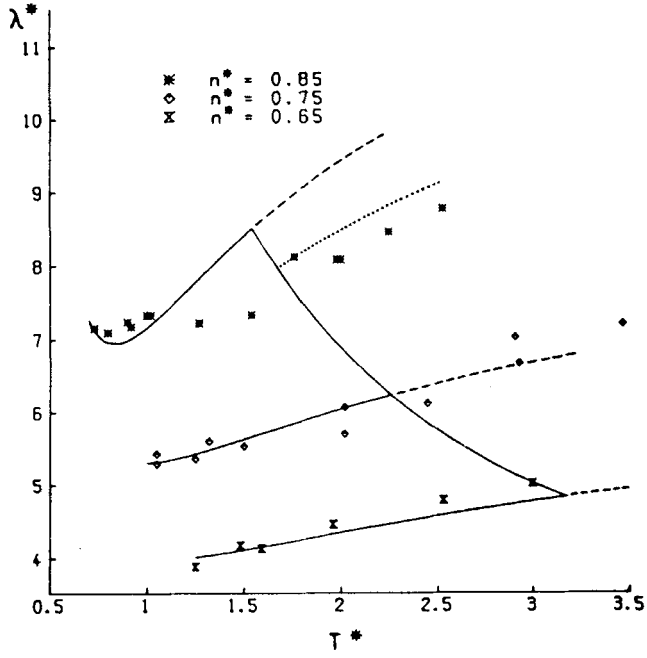

Figure 2 As in Figure 1, but for the thermal conductivity. The dotted line indicates an extrapolation of the fit curve for $n^* = 0.83$. The descending line corresponds to state points of about 200 MPa.

equation. However, as opposed to the shear viscosity, for the thermal conductivity there exist no experimental data, which could be directly compared with. In Figure 2 we show also the extrapolated experimental fit curve for $n^* = 0.83$ (dotted curve). The more linear form appears to us to have the correct tendency for higher temperatures which should hold also for the density of $n^* = 0.85$.

We conclude that the Lennard-Jones potential may satisfactorily be used to describe both the shear viscosity and the thermal conductivity of real argon over a wide range of dense thermodynamic states including the triple point.

5 FINAL REMARKS

We have shown that MD calculations based on the Lennard-Jones pair potential give the transport coefficients and in very good agreement with experiment for an extended range of densities and temperatures.

Unfortunately there are no experimental bulk viscosity data of that quality for argon which could be used for comparisons with MD results. However, even if the bulk viscosity could be measured accurately, a comparison with MD predicted values seems to be difficult for states in the neighbourhood of the triple point of argon. At these states the bulk viscosity coefficient is underestimated by MD calculations of 10^5 time steps. Accurate MD results for this coefficient would require much longer runs.[8,9].

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Appendix

The fit equations used by Younglove and Hanley[7] to correlate the experimental values of the shear viscosity η_s and the thermal conductivity λ are of the following form:

$$\eta_s(\rho, T) = \eta_0(T) + \Delta\eta_s(\rho, T)$$
$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T),$$

where the $\Delta\lambda$ and $\Delta\eta_s$ terms account for the density dependence of the coefficients, and $\lambda_c(\rho, T)$ accounts for the critical enhancement. η_0 and λ_0 are the dilute gas values, and ρ and T denote density and temperature.

For $\Delta\eta_s$ and $\Delta\lambda$, Younglove and Hanley selected the following form:

$$\Delta\eta_s = \sum_{i=1}^{4} f_i \rho^i/(1 + f_5\rho)$$

$$\Delta\lambda = \sum_{i=1}^{4} t_i \rho^i/(1 + t_5\rho)$$

where the f_i, f_5, t_i, t_5 are certain fit parameters and ρ^i denotes the ith power of ρ. Using a correlation length parameter of $\Xi = 6.0795 \times 10^{-10}$m (see Table 4 of Ref. 7) the values of Tables 6 and 7 in Ref. 7 were reproducible within the given digits.