Shear Properties of Liquid Methane

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Abstract: Shear modulus, shear stress, shear waves speed, travel time of shear waves and work done by a diffusing atom of methane were determined by using thermodynamic relations in which the thermodynamic quantities were obtained from molecular dynamic simulations. The atoms were modeled by Lennard-Jones (LJ) pair potential. The shear modulus, shear stress and shear waves speed decrease as temperature increases and density decreases. The shear waves take longer time to travel at lower densities. The work done by a diffusing atom of methane decreases as the rate of diffusion of atoms increases. Good agreement between prediction from simulation and experimental data is found for shear modulus at T=90.7K.

Keywords: Molecular dynamics simulations; Shear modulus; shear stress; Methane; Shear waves.

1. INTRODUCTION

Green-Kubo Methane is an important fuel. Being the simplest hydrocarbon, the combustion of methane produces more heat per gram than other hydrocarbons. Liquid methane is used as rocket fuel [1]. The knowlegde of the shear properties of liquid methane is essential because shear modulus of liquids can be applicable in coating and detection of changes in colour, density and molecular weight in the chemical industry e.g. in reactor for polymerization.

The transport and thermodynamic properties of methane were studied with Monte-Carlo (MC) [2]-[4] and Molecular Dynamics (MD) [5]-[9] simulations. X-rays scattering of liquid methane were studied [10]-[12]. X-ray diffraction studies of solid methane were carried out [13]. Stahl and his coworkers investigated the velocity of longitudinal high-frequency sound in solid methane and the temperature dependence of the velocity [14]. Methane in a model silica gel and in water were studied [15], [16].

Shear properties are found in solids most often. And so most calculations on shear properties in the literatures were performed on solid systems. At higher densities, liquids exist in the elastic regime behaving like solids. So at higher densities, shear properties are observed in liquids.

However shear properties of liquids are still not very much studied in details. A knowlegde of the shear properties of liquids particularly simple fluid like methane is essential considering its high technological importance.

In this work, we investigated the effects of temperature and density on the shear properties of liquid methane such as shear modulus, shear stress, shear waves speed and work done by a diffusing atom of methane. The shear modulus are calculated using an analytic relation which involves pressure and internal energy [17]. The latter are obtained directly from simulation data. The diffusion coefficient is calculated using the Gree-Kubo relation.

2. SIMULATION METHOD

The atoms of methane interact with the Lennard-Jones(12-6) pair potential [18].

$$u(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \tag{1}$$

Where σ and ε are the units of length and energy respectively.

The inter-particle forces are calculated from the Lennard-Jones potential. forces are evaluated using MD integrator to generate atomic trajectories. From these trajectories, thermodynamic properties such as pressure, internal energy and pair distribution function obtained are used to calculate the shear properties.

The pair distribution function, g(r) can be calculated from simulation data using:

$$g(r) = \frac{\langle N(r, \Delta r) \rangle}{\frac{1}{2} N \rho V(r, \Delta r)}. \tag{2}$$

N(r,Δr) is the number of atoms found in a spherical shell of radius r and thickness Δr with the shell centered on another atom. V (r,Δr) is the volume of the spherical shell. N is the total number of atoms.

The internal energy is the average of the pair potential and it is given as

$$U_i = 2\pi\rho \int_0^\infty r^2 g(r) u(r) dr \tag{3}$$

To calculate the pressure, we use:

$$P = \rho T - \frac{2}{3}\pi\rho^2 \int_0^\infty r^3 g(r) \frac{du(r)}{dr} dr \tag{4}$$

The Green-Kubo relation gives the diffusion coefficient as:

$$D = \int_0^\infty <v(\tau)v(0)> d\tau \tag{5}$$

Where $\tau = t - t'$ and $<v(\tau)v(0)>$ is a measure of the correlation between the velocity of an atom at time τ and t=0 and it is known as the velocity autocorrelation function.

Shear waves are tranverse waves which move through the body of a system unlike surface waves. Shear waves occur in solids most often. At low frequency, liquids support only longitudinalwaves (surface). At higher frequency or density, the dynamical properties of liquids move from the hydrodynamic regime (liquid-like or viscous behaviour) to the elastic regime (solid-like behaviour). So at higher frequency or density, shear waves are observed in liquids [18]. At this point, resistance to deformation of liquids characterized by two elastic constants; the bulk modulus (the inverse isothermal compressibility) and the shear modulus (coefficient of rigidity) [19].

For the Lennard-Jones substance, the shear modulus G is related to thermodynamics by [17]

$$G = 3P - \frac{24}{5}\rho U_i - 2\rho K_B T \tag{6}$$

Where P and U_i are the pressure and the configurational internal energy respectively.

The work done by a diffusing particles to shove other neighbouring particles is given as [20]

$$W = GV \tag{7}$$

Where V is the volume of the simulation box.

Shear stress is given as the product of the shear viscosity and the velocity gradient

$$\tau = \eta \nabla v \qquad (8)$$

Using the Einstein's relation, shear stress is related to the diffusion coefficient as;

$$\tau = \frac{K_B T <v>}{6\pi r D L} \qquad (9)$$

Shear stress arises from the force acting parallel to the liquid.

The shear force acting on the liquid generates shear waves with a shear velocity given as [21]

$$v = \sqrt{\frac{G}{\rho}} \qquad (10)$$

The travel time of the shear waves generated is given by;

$$t = \frac{L}{v} \qquad (11)$$

Where L is the length of the simulation box.

The equations of motion were solved using the leap-Frog integration scheme with a constant time step algorithm (Δt = 0.004). Periodic boundary conditions around the central cubic box and the minimum image truncation were included in the calculations. Long-range corrections were also applied [22]. Simulations were performed at high temperatures and densities at and above the melting point of the system. Interactions beyond distance $r_c = L/2$ are set to zero, where r_c is the cut-off radius and L is the length of the simulation box.

The input parameters for the Lennard-Jones model are σ = 3.743Å and ε = 149.1K [23].

3. RESULTS AND DISCUSSION

TABLE I: THERMODYNAMIC STATE POINTS OF METHANE

T(K)	T*	ρ(g/cm^3)	ρ^*
90.7	0.608	0.5384	1.060
99.8	0.669	0.4407	0.868
110.9	0.744	0.4253	0.837
116.5	0.781	0.4173	0.822
122.1	0.819	0.4091	0.805
125.0	0.838	0.4005	0.788

TABLE II: CALCULATED THERMODYNAMIC PROPERTIES OF METHANE

T*	ρ^*	U_i^*	P*
0.608	1.060	-6.731	7.707
0.669	0.868	-6.056	0.566
0.744	0.837	-5.797	0.497
0.781	0.822	-5.692	0.366
0.819	0.805	-5.554	0.333
0.838	0.788	-5.423	0.263

TABLE III: CALCULATED SHEAR PROPERTIES OF METHANE

T(K)	ρ (g/cm^3)	G$_{md}$(GPa)	G$_{expt}$(GPa)	T(10^{7}Pa)
90.7	0.5384	2.20	2.00	6.09
99.8	0.4407	1.01	—	1.63
110.9	0.4253	0.92	—	1.28
116.5	0.4173	0.87	—	1.14
122.1	0.4091	0.83	—	1.11
125.0	0.4005	0.78	—	0.97
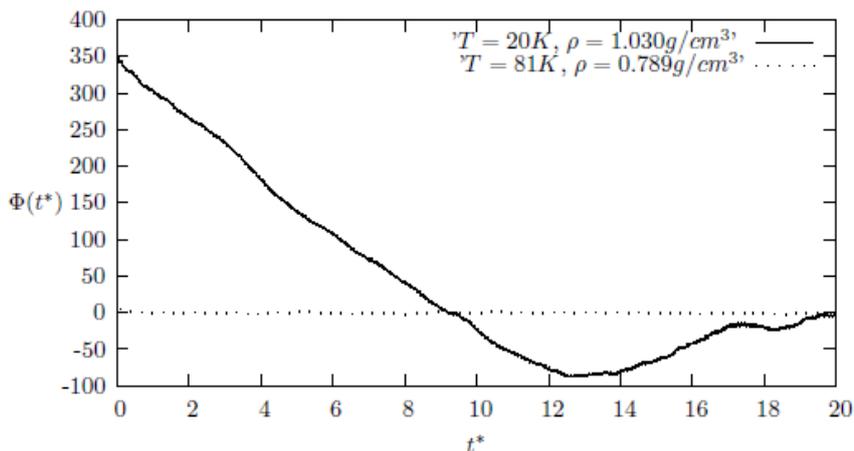
Fig. 1: Stress autocorrelation function of Nitogen at solid and liquid states
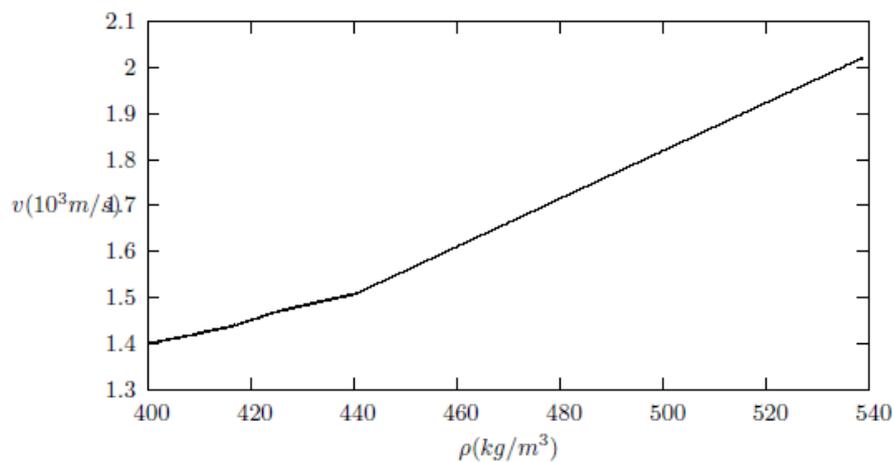

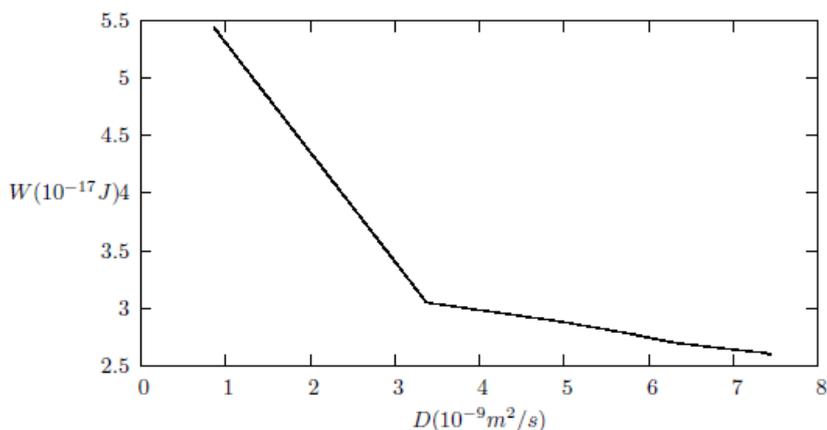Fig. 2: Shear waves speed of methane at the investigated densities

Figure 3: Variation of work done by a diffusing atom of methane with diffusion coefficient
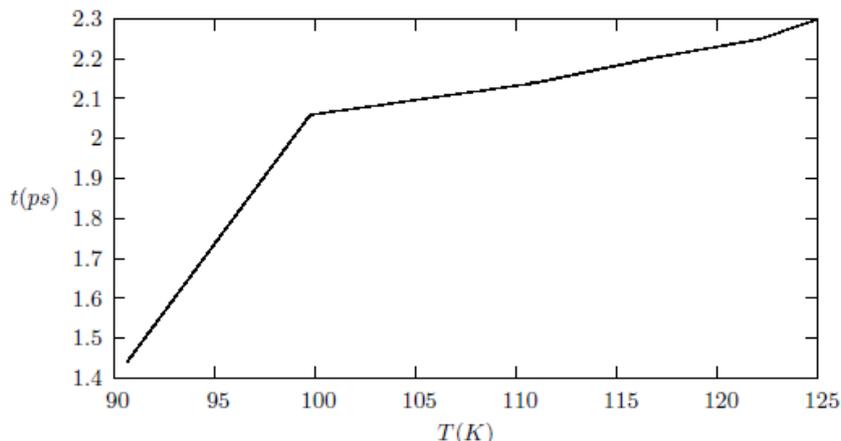
Fig. 4: Time of travel of the shear waves in methane as a function of temperature

Table 1 shows the thermodynamic state points of methane used for calculations in this work. The sets of temperatures and densities used are taken from the literature [24].

Table 2 presents the thermodynamic properties of methane. The internal energy increases with temperature while the pressure decreases as temperature increases. The reduced quantities used are: $\rho^*=\rho\sigma^3$, $T^*=K_BT$, $U_i^*=U_i/N\varepsilon$ and $P=P\sigma^3/\varepsilon$ density, temperature, internal energy and pressure respectively.

The shear properties are presented in Table 3. The shear modulus, shear stress and shear waves speed decrease as density decreases and temperature increases. The calculated shear modulus of solid methane at at 90.7k compared favourably with experiment [25].

Stress autocorrelation function generated in time is presented in fig. 1. The solid line represents the graph for solid methane at T=90.7K while the broken lines represents liquid methane at T=125.0K. For liquid methane, the decay of this function is faster because of the increase in the number of scattering processes. For solid methane, the decay is slower due to rebounding motion at this temperature.

At high densities, atoms are closely packed so that rebounding collisions are more numerous and the many rebounds cause instability at T=90.7K and $\phi(t^*)$ goes below zero. At low density, collisions scatter atoms without changing their trajectories, therefore $\phi(t^*)$ fluctuate about zero at T=125.0K.

Fig. 2 presents the graph of shear waves speed against density. As density increases, the speed of the shear waves increases. This implies that the generation of shear waves are density dependent.

Fig. 3 shows the variation of work done by a diffusing atom with diffusion coefficient. As diffusion coefficient increases, the work done decreases. At high temperature, the rate of dif fusion is also high and so the work done by a diffusing atom to push aside neighbouring atoms is low.

The travel time of the shear waves generated in methane as a function of temperature is presented in fig. 4. The time taken for shear waves to travel through the length of the simulation box increases as temperature increases.

4.   CONCLUSIONS

In the present work, Molecular dynamics simulations were used to calculate thermodynamic properties for liquid methane. The calculated thermodynamic properties are pressure and internal energy. The atomic interactions of methane were modeled by the Lennard-Jones potential. The study covers temperature in the range 90.7k to 125.0K and density in the range 0.4005g/cm^3 to 0.5384g/cm^3. The diffusion coefficients were determined by Molecular dynamics simulations with the Green-Kubo method. The shear properties were obtained using thermodynamic relations with thermodynamic properties obtained directly from simulation data. The shear properties are directly proportional to the density. As density increases, shear properties also increase. This implies that shear properties vanishes as density tends to zero. As density decreases, the shear waves travel time increases. As the rate of duffusion increases, a diffusing atom does lesser work to shove aside neighbouring atoms. A comparison with available experimental data shows good agreement for shear modulus of methane at the solid temperature of 90.7k. To the best of our knowledge, no experimental data on other shear

properties are available in the literatures. We are satisfied to discuss our results considering the absence of experimental studies on these properties for methane at the investigated state points. Hence, our results can serve as a prediction for future investigations. Also, it is worthwhile to extend the study to more complex fluids.

ACKNOWLEDGEMENTS

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