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Elastic and Kinetic Properties of liquid Nitrogen

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Abstract: *The elastic and kinetic properties of liquid nitrogen have been calculated using Molecular Dynamics (MD) computer simulations. The interactions of the atoms were approximated by the Lennard-Jones (LJ) pair potential. Shear modulus (coefficient of rigidity), bulk modulus (inverse isothermal compressibility), shear waves speed and kinetic properties (work done by a diffusing atom) were calculated by analytic expressions using direct simulation data for the thermodynamic quantities. The thermodynamic quantities are pressure and internal energy. The shear modulus and bulk modulus decrease as temperature increases but increase with density. The speed of the shear waves generated in nitrogen decreases as investigated density decreases. The work done by a diffusing atom of nitrogen also decreases with density. Elastic and kinetic properties of nitrogen are directly proportional to density making the properties to be more pronounced in solid state. The shear modulus ranges from 0.63GPa to 1.37GPa while the bulk modulus ranges from 1.02GPa to 2.44GPa at the investigated temperatures and densities. At temperature of 20K, the bulk modulus of solid nitrogen compared well with experimental values with small discrepancy.*

Keywords: *Molecular dynamics simulations; Shear modulus; Bulk modulus; Nitrogen; Shear waves*

1. INTRODUCTION

The bulk modulus of fluids is a widely used quantity in the exploration and production of fluid reservoirs. In chemical and thermal process engineering, knowledge of elastic properties of pure substances and mixtures is essential. The vapour pressure of nitrogen has been measured in the liquid range below the normal boling point and above [1,2]. X-rays scattering of liquid nitrogen [3] were studied. Thermodynamic, structural, and transport properties of nitrogen were studied and compared with both experimental data and recent theoretical investigations [4]. New formulations for the viscosity and thermal conductivity for nitrogen, oxygen, argon, and air has been given [5]. Waterman presented a theory for calculating the shear modulus of a surface layer on liquids bovine and sodium casseinate [6]. Granato investigated the shear modulus of liquid glasses using the interstialcy model [7]. Expressions for the elastic modulus tensor for fluids and solids have been presented [8]. The frequency dependence of the elastic and loss modulus of a hard sphere dispersion, electrostatically and electrosterically stabilized particles, worm-like micelles, polystyrene microgels, and polymer solutions was studied [9]. Maggi and his coworkers reported shear modulus measurements for five glass-forming liquids (pentaphenyl trimethyl trisiloxane, diethyl phthalate, dibutyl phthalate, 1,2-propanediol, and m-touluidine) obtained by the piezoelectric shear-modulus gauge (PSG) method [10]. Kotakoski and Albe compared various solid nitrogen phases by means of ab initio calculations based on density-functional theory to describe solid nitrogen at different pressures [11]. Schappert and Pelster showed that solid nitrogen has considerably enhanced elastic properties in the nanopores of a porous glass [12]. It is generally accepted that the shear modulus of a liquid is zero. Many theories of melting are based on this supposition. But this is not true. The interstitialcy model [13] predicts that the shear modulus of a liquid is not zero. A few calculations on amorphous substances near the glass temperature are available which show equilibrium effects which can be readily understood with this model in terms of the liquid state shear modulus. The fact that fluids do flow and solids do not is usually associated to the vanishing or non-vanishing of the shear modulus. Yet the Born-Green expression for the shear modulus is accurately determined [14-16] and yields non-zero values even for the fluid state [17].

In this work, we investigated the effects of temperature and density on shear modulus and other elastic properties of liquid nitrogen such as bulk modulus, shear waves speed and work done by a diffusing atom of nitrogen. The shear and bulk moduli were calculated using the theory that linked the elastic properties to the pressure and internal energy [17]. MD simulation is used to calculate the pressure. and internal energy.

2. COMPUTATIONAL METHOD

The Lennard-Jones (12-6) pair potential [18] is used to model the interactions of atoms in nitrogen.

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

Where σ is the atomic diameter, ε is the LJ energy parameter and r_{ij} is the interatomic distance between atoms i and j.

The forces on all atoms are determined from the atomic interactions. Newton's equation of motion is used to obtain atomic positions, velocities and accelerations. From these trajectories, thermodynamic properties such as pressure, internal energy and pair distribution function obtained are used to calculate elastic properties.

The g(r) measures how atoms organize themselves around one another. It is proportional to the probability of finding two atoms seperated by distance r+Δr. The g(r) can be simply evaluated from simulation data using:

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

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

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

To calculate the pressure, we use:

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

When water surface is striked with the blade of a paddle, the water's initial response to the sudden shock is a resistance to deformation much like that of a solid, resistance characterized by two elastic constants; the bulk modulus (the inverse isothermal compressibility) and the shear modulus (coefficient of rigidity) [19]. It is because of water's elastic resistance to a suddenly applied force that, if thrown hard and at low angle, a stone will skip across a lake's surface.

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

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

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

The bulk modulus B is given as [17]

$$B = \frac{5}{3} G + 2(P - \rho T) \tag{6}$$

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.

The shear force acting on the liquid generated a shear wave with a shear velocity given as [21]

$$u = \frac{G}{\rho} \tag{8}$$

All simulations were performed in a cubic box of volume V with periodic boundary condition in all the three dimensions containing N = 500 atoms of nitrogen. Simulations were performed at high temperatures and densities at and above the melting point of the nitrogen. The equation of motion for the atoms were integrated using the Leap frog algorithm with a time step of 0.004. Interactions beyond distance r_c = L/2 are set to zero, where rc is the cut-off radius and L is the length of the simulation box. Where necessary correction terms were estimated and added by using Ewald summation method [22]. The input parameters for the Lennard-Jones model are σ = 3.636Å and ε = 101.6K [23].

3. RESULTS AND DISCUSSION

Table 1 shows the thermodynamic state points of nitrogen used for calculations in this work. The sets of temperatures and densities used are taken from the literatures [2,24]. As temperature increases, density decreases. The thermodynamic properties of nitrogen are presented in Table 2. While the pressure decreases, the internal energy increases with temperature. The reduced quantities used are: $\rho^*=\rho\sigma^3$, $T^*=K_BT$, $U_i^*=U_i/N\varepsilon$ and $P=P\sigma^3/\varepsilon$.

In table 3, the shear modulus and bulk modulus of nitrogen are observed to decrease with increasing temperature. The calculated bulk modulus of solid nitrogen (Gmd) at T= 20K compared well with the experimental value (Gexpt) [25] within 13% error.

Stress autocorrelation function generated in time is presented in figure 1. The solid line represents the graph for solid nitrogen at T=20K while the broken lines represents liquid nitrogen

at T=81K. For liquid nitrogen, the decay of this function is faster because of the increase in the number of scattering processes. For solid nitrogen, 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 than scattering collisions and the many rebounds cause instability at T=20K and so, the stress autocorrelation function, $\phi(t^*)$, goes through a minimum before approaching zero. At low density, collisions scatter atoms without changing their trajectories, therefore $\phi(t^*)$ become positive at T=81K.

Figure 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 is density dependent.

Figure 3 shows the variation of work done by a diffusing atom with temperature. As temperature increases, the work done decreases. At high temperature, less work is required by a diffusing atom to push aside neighbouring atoms.

Table1. *Thermodynamic State Points of Nitrogen*

T(K)	T^*	ρ(g/cm^3)	ρ^*
20.0	0.197	1.030	1.065
63.2	0.622	0.870	0.899
66.0	0.650	0.857	0.886
77.0	0.758	0.808	0.835
81.0	0.797	0.789	0.815

Table2. *Calculated Thermodynamic Properties of Nitrogen*

T^*	ρ^*	U_c^*	P^*
0.197	1.065	-7.621	2.851
0.622	0.899	-6.296	0.783
0.650	0.886	-6.190	0.721
0.758	0.835	-5.790	0.441
0.797	0.815	-5.657	0.219

Table3. *Calculated Elastic Properties of Nitrogen*

T(K)	ρ (g/cm^3)	G(GPa)	B(GPa)	B_{expt}(GPa)
20.0	1.030	1.37	2.44	2.16
63.2	0.870	0.83	1.39	—
66.0	0.857	0.80	1.34	—
77.0	0.808	0.68	1.12	—
81.0	0.789	0.63	1.02	—

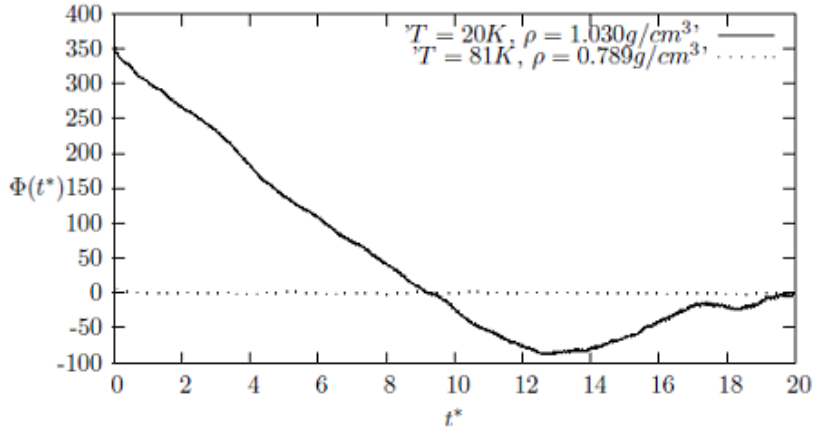

Figure1. *Stress autocorrelation function of Nitogen at solid and liquid states*

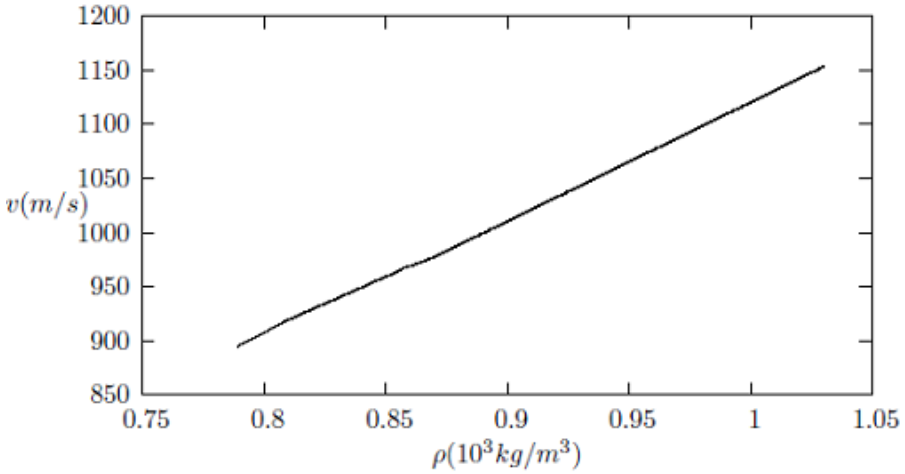

Figure2. *Speeds of shear waves in Nitrogen at the investigated densities*

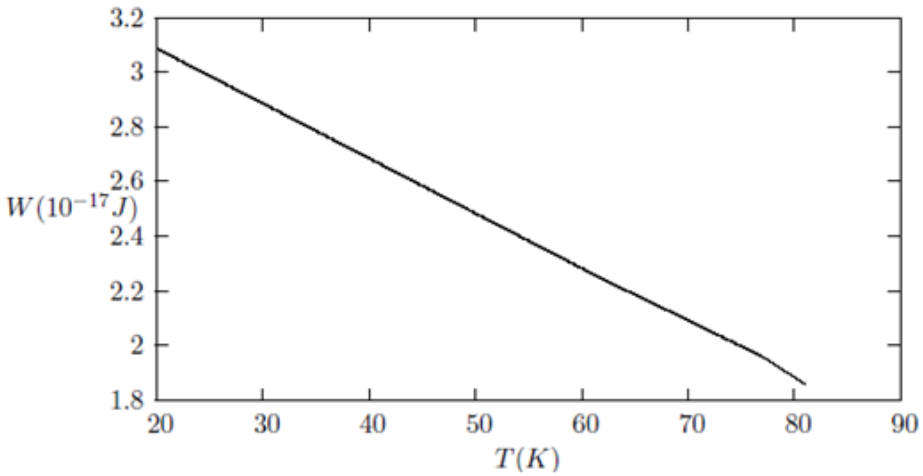

Figure3. *Work done by a diffusing particle of Nitrogen*

4. CONCLUSIONS

We have performed MD simulations to investigate the elastic and kinetic properties of nitrogen and the effects of temperature and density on them. Lennard-Jones pair potential was used to model nitrogen. The shear modulus and bulk modulus have been determined by using thermodynamic relations. For the thermodynamic quantities, we used direct simulation values. The elastic properties are directly proportional to the density. As density increases, elastic properties also increase. This implies that elastic properties approach zero as low density. As temperature increases, a diffusing atom does less work to shove aside neighbouring atoms. The relation for shear modulus gives non-zero values for liquid state at T=63.15K to T=81K. The experimental results on the elastic properties of solid Nitrogen at T=20K compared well with the calculated results and so MD simulation method

is reliable and efficient for the calculation of thermodynamic and elastic properties of simple fluids such as nitrogen. The method can be used to investigate the elastic propeties of compounds and pastes.

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