

Adhesion energy, surface traction and surface tension in liquid xenon

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Abstract. We calculated the adhesion energy, the surface traction and the surface energy of liquid xenon using molecular dynamics (MD) simulation. The value of the adhesion energy for liquid xenon at a reduced density of 0.630 was found to be 0.591 J/m² and the surface traction has a peak at $z = 3.32$ Å. It was observed that the attraction of the molecules in the liquid surface which produces a resistance to penetration decreases with temperature. This may be attributed to the greater average separation of molecules at higher temperature.

Keywords. Molecular dynamics simulations; diffusion coefficient; viscosity; Lennard–Jones potential; xenon.

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1. Introduction

Liquified rare gases under pressure, particularly xenon, are employed as solvents in infrared spectroscopy. The gases are useful for this purpose because they are transparent to infrared radiation and therefore do not obscure the spectra of the dissolved substance.

Spectroscopists are interested in how the temperature affects the separation technique. So, it is necessary to study the thermophysical properties of xenon.

A number of researchers studied the three transport properties; diffusion coefficient, shear viscosity and thermal conductivity of rare gases using Lennard–Jones potential [1–8], yet others have used an *ab initio* parametrized potential and semi-empirical pair potential [9,10] and some used three-body interaction potential [11,12]. The adhesion energy, surface traction and surface tension of Fe–Mg alloys were calculated using molecular dynamics simulation [13]. The structural information as well as the calculated surface tension suggest segregation in Fe–Mg alloys at all investigated temperatures.

The present work is organized in the following order: in §2 we explain the theoretical method used in our calculations. In §3 we give detailed results and a discussion of the findings of this work and in §4 we present the conclusions.

2. Computer simulations

Molecular dynamics simulations generate information at the microscopic level including atomic positions and velocities by solving the equation of motion of the interacting particles numerically. The connection between microscopic simulations and macroscopic properties is made via statistical mechanics which provides rigorous mathematical expressions that relate the macroscopic properties to microscopic observables. We performed our simulations in a cubic box of volume V containing $N = 864$ atoms of xenon with periodic boundary condition in three dimensions. Calculations were done at temperatures 281, 314, 344, 405 and 473 K, corresponding to reduced temperatures of 1.232, 1.377, 1.509, 1.776 and 2.075 K respectively, and at a density of 177 mol/dm^3 (0.630 in reduced unit). The reduced density and the reduced temperature are given as $\rho^* = \rho\sigma^3$ and $T^* = K_B T/\epsilon$ respectively.

A good starting point for any MD simulation is the selection of a potential function to mimic the system of interest. Potential and forces on atoms are calculated at a time step of $\Delta t = 0.004$. The equation of atomic motion is solved numerically using the Verlet algorithm [14]. The trajectories obtained from the integration are used to calculate the dynamical and static properties of interest.

The mass m of an atom was set to unity for convenience, while the interactions beyond the cut-off radius $r_c = \frac{1}{2}L$ are set to zero, and correction terms are added where needed. L is the length of the simulation box. The pairwise potential used in the present work is the LJ 12-6 potential given by

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

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 force between two atoms may be written as

$$F = -\frac{dV(r)}{dr} = -24\frac{\epsilon}{\sigma} \left[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^7 \right]. \quad (2)$$

By convention, repulsive forces are positive while attractive forces are negative. The pair distribution function is given by

$$g(r) = \frac{n(r)}{\Delta r \rho}, \quad (3)$$

where $n(r)$ is the average number of atoms that can be found in a shell within the distance $r - \frac{\Delta r}{2} < r < r + \frac{\Delta r}{2}$ and Δr is the shell thickness.

In macroscopic systems, we can represent the atomic interactions between atoms by surface traction [15] and by assuming the surface traction to be in the z -direction. Then for a LJ potential one can write the surface traction [16] as

$$T_0(z) = \frac{A}{6\pi z_0^3} \left[\left(\frac{z_0}{z} \right)^3 - \left(\frac{z_0}{z} \right)^9 \right] \quad (4)$$

which is

$$= \frac{8\Delta\gamma}{3z_0} \left[\left(\frac{z_0}{z} \right)^3 - \left(\frac{z_0}{z} \right)^9 \right] \quad (5)$$

Table 1. Lennard–Jones parameters for xenon used in this work.

System	σ (Å)	ϵ_B (K)
Xenon	3.9	228

where A is known as the Hamakar constant [17] and is defined as

$$A = 4\epsilon\pi^2\rho^2\sigma^6, \quad (6)$$

where ρ is the density of the system.

The surfaces of two atoms are in equilibrium when $T_0 = 0$, which means the equilibrium distance z_0 is written as

$$z_0 = \left(\frac{2}{15}\right)^{1/6} \sigma. \quad (7)$$

We can now define $\Delta\gamma$ as the adhesion energy between the surface of the two atoms in contact, which is the work done to move two surfaces from equilibrium separation z_0 to infinity.

$$\Delta\gamma = \int_{z_0}^{\infty} T_0(z)dz = \frac{A}{16\pi z_0^2}. \quad (8)$$

Both the liquid–vapour surface tension and viscosity are related by the equation [18]

$$\eta(T) = \frac{16\beta_{lv}(T)}{15} \sqrt{\frac{M}{N_A K_B T}} \quad (9)$$

which is

$$= \frac{16\beta_{lv}(T)}{15} \sqrt{\frac{m}{K_B T}} \quad (10)$$

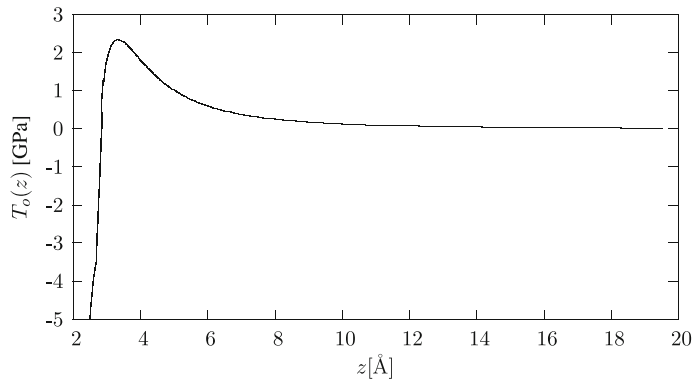


Figure 1. Atomic interactions between atoms in liquid Xe.

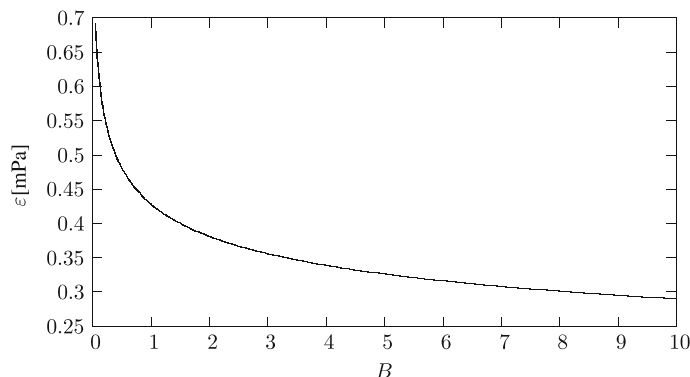


Figure 2. A variation of the effective elastic modulus ϵ of liquid Xe as a function of B .

or by the diffusion coefficient

$$D(T) = \frac{5K_B T}{32\pi r \beta_{lv}(T)} \sqrt{\frac{M}{N_A K_B T}}, \quad (11)$$

where N_A , M and K_B are respectively, the Avogadro's number, atomic mass and Boltzmann's constant.

From the pair distribution function $g(r)$, it is possible to calculate the coordination number C_n in the first shell. The first shell can be defined in several ways, but we have used the position of first minimum r_m to define the first shell in our calculations [19].

$$C_n = 4\pi \int_0^{r_m} \rho(r) r^2 g(r) dr. \quad (12)$$

If we use the Maugis theory [20], we see that a dimensionless parameter

$$B = 1.03 \frac{\Delta\gamma}{z_0} \left(\frac{9R}{2\pi \Delta\gamma \epsilon_B^2} \right)^3 \quad (13)$$

allows to comment on the effective elastic modulus ϵ_B of the constituent atoms:

$$\epsilon_B = \sqrt{\left(\frac{1.03 \Delta\gamma}{z_0 B} \right)^{1/3} \sqrt{\frac{9R}{2\pi \Delta\gamma}}}, \quad (14)$$

where $R = \sigma^2/4\sigma = \sigma/4$ is the contact radius. It is worth mentioning that B can be seen as a measure of the ratio of elastic deformation to the effective range over which the surface traction is valid.

Table 2. Calculated structural properties of liquid Xe.

T (K)	r_0/σ	r_{\max}/σ	r_{\max}/r_0	$g(r_{\max})$	$g(r_{\min})$	C_n
281	1.6110	1.0999	0.68	2.1615	0.7894	8.7131
314	1.6332	1.0777	0.66	2.1113	0.8011	9.2134
344	1.6332	1.0777	0.66	2.0799	0.8052	9.2598
405	1.6332	1.0777	0.66	2.0084	0.8180	9.4079
473	1.6332	1.0777	0.66	1.9516	0.8283	9.5260

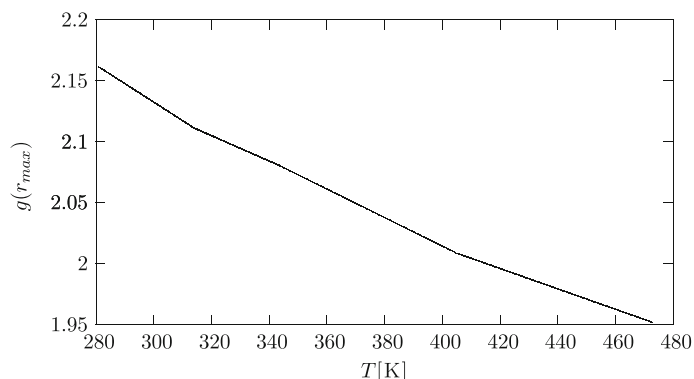


Figure 3. Plot of the principal peaks in the effective pair distribution function for liquid Xe.

3. Results

The parameters of the LJ potential for xenon used in this work are given in table 1. The parameters are taken from [21]. The adhesion energy holding atoms together calculated using eq. (8) in xenon was found to be 0.591 J/m^2 .

Figure 1 shows the curve of the surface traction in Xe with a peak occurring at $z_0 = 3.32 \text{ \AA}$. From the plot, it is seen that the attractive force between the surfaces has a constant value at a gap less than a certain separation and goes to zero at large separations. Figure 2 shows the relationship between the effective elastic modulus ϵ and B . The effective elastic modulus decreases as B increases.

In table 2, we present the states of the system studied and the structural information from our calculations. The sets of temperatures used are taken from experimental data [22,23]. We determine the symmetric distance ratio r_{\max}/r_0 . An average value of 0.66 was obtained. It was observed that the coordination number increases with increasing temperature. A possible reason for this behaviour could be that the separation of pairs of atoms is happening in the first shell as the temperature increases. Hence, separation of pairs of atoms leads to overcrowding in the first shell resulting in an increased number of nearest neighbours in the first shell.

Figure 3 shows the variation of $g(r_{\max})$ with temperature. As T increases, the main peak in the effective pair distribution function decreases.

Table 3 shows the calculated dynamic coefficients from our studies.

Table 3. Calculated dynamical properties of liquid xenon.

T (K)	D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	η (m Pa.s)	β_{IV} (10^{-5} Nm^{-1})
281	8.8977	0.1287	0.083
314	9.7620	0.1393	0.080
344	10.5871	0.1795	0.077
405	12.2050	0.2296	0.073
473	14.3255	0.3956	0.067

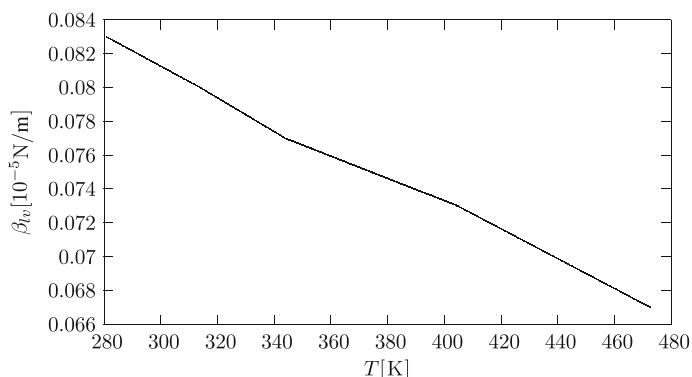


Figure 4. Surface tension in liquid Xe at the investigated temperatures.

The diffusion coefficient (D) and the shear viscosity increase with temperature. Looking at figure 4, the surface tension in liquid xenon decreases with temperature.

4. Conclusions

We used the interatomic Lennard–Jones potential to determine the adhesion energy and surface traction in liquid xenon over the temperature range of 281–473 K at a density of 177 mol/dm^3 . The adhesion energy of liquid Xe depends on density. The calculated surface traction has a peak at $z = 3.32 \text{ \AA}$. The calculated structural and dynamical quantities are in agreement with the theory.

The surface tension of liquid xenon decreases with temperature and hence the force of attraction between molecules on the surface of the liquid decreases. It is worthwhile to investigate the relationship that exists between the surface tensions and the boiling points of simple fluids and molecular liquids.

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