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A molecular dynamics study on the role of attractive and repulsive forces in internal energy, internal pressure and structure of dense fluids

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Abstract

Isotherms of experimental data of internal pressure of dense fluids versus molar volume, V_m are shown to have each a maximum point at a V_{max} below the critical molar volume. In this study, we investigated the role of attractive and repulsive intermolecular energies on this behavior using a molecular dynamics simulation technique. In the simulation, we choose the Lennard-Jones (LJ) intermolecular potential energy function. The LJ potential is known to be an effective potential representing a statistical average of the true pair and many-body interactions in simple molecular systems. The LJ potential function is divided into attractive and repulsive parts. MD calculations have produced internal energy, potential energy, transitional kinetic energy, and radial distribution function (RDF) for argon at 180 K and 450 K using LJ potential, LJ repulsive, and LJ attractive parts. It is shown that the LJ potential function is well capable of predicting the inflection point in the internal energy-molar volume curve as well as maximum point in the internal pressure-molar volume curve. It is also shown that at molar volumes higher than V_{max}, the attractive forces have strong influence on determination of internal energy and internal pressure. At volumes lower than V_{max}, neither repulsive nor attractive forces are dominating. Also, the coincidence between RDFs resulting from LJ potential and repulsive parts of LJ potential improves as molar volume approaches V_{max} from high molar volumes. The coincidence becomes complete at $V_{max} \geqslant V$.

Keywords: Internal pressure; Molecular dynamics; Dense liquids; Lennad-Jones potential; Radial distribution function

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1. Introduction

According to statistical mechanics, the internal energy of a body, E, consist of the sum of the kinetic energies, KE(T), of molecules comprising the system due to molecular motions plus intermolecular attractive, U_A, and repulsive, U_R, energies [1]:

$$E = \mathrm{KE}(T) + U_A + U_R, \tag{1}$$

$$U = U_A + U_R, \tag{2}$$

where U is the total intermolecular potential energy of the body. Differentiation from Eq. (2) with respect to volume at constant temperature gives:

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U_A}{\partial V}\right)_T + \left(\frac{\partial U_R}{\partial V}\right)_T. \tag{3}$$

The state function $\left(\frac{\partial U}{\partial V}\right)_T$ in Eq. (3) has dimensions of pressure and it is called the internal pressure, P_i. Eq. (3) can then be written as

$$P_i = P_{iA} + P_{iR}, \tag{4}$$

where P_{iA} and P_{iR} are internal pressure resulting from attractive and repulsive intermolecular interactions, respectively.

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Clearly, P_i, is related to that part of the internal energy that is due to intermolecular potential energies. Internal pressure, is a fundamental property of a substance which is closely related to its different properties such as ultrasonic velocity, free volume, surface and interfacial tensions, solubility parameter, and latent heats of phase transitions (like vaporization in of liquids) [2].

The internal pressure values are significant in the evaluation of thermodynamic properties of substances. A general method of calculating the internal pressure is based on the thermodynamic equation of state,

$$P_i = \left[\frac{\partial U}{\partial V}\right]_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \qquad (5)$$

There has been an increasing interest in the measurement or calculation of internal pressure in the elucidation of thermodynamic properties of condensed matter including liquids and liquid mixtures since it gives the resultant forces of attraction and repulsion [3]. This feature of internal pressure is of important significance because it provides valuable information on attractive and repulsive intermolecular forces.

The purpose of this study is to investigate the role of attractive and repulsive intermolecular energies on behavior of internal pressure using a molecular dynamics simulation. It happens that internal energy of condensed matter also has an anomalous point as the internal pressure. In this study, the structure of the condensed matter through the radial distribution function around the internal pressure maximum point will be also investigated.

2. The behavior of isotherms of internal pressure and internal energy versus volume

Isotherms of internal energy, E, of liquids versus molar volume, V, at fixed temperature are shown to have inflection points and the isotherms of the internal pressure are shown to have maximum points [2]. We have used the experimental PVT data of liquid argon, liquid krypton, and liquid xenon for which extensive reliable data are available [4–6]. For these liquids, we have calculated and plotted the internal pressure versus molar volume at various temperatures. We interestingly notice that the isotherms of internal pressure versus molar volume for all the liquids studied have a maximum at a molar volume (we call V_{max}) below the critical molar volume. For example for argon, where $P_c = 48.6$ atm, $T_c = 150.7$ K and $V_c = 0.048$ L mol^{-1}, the isotherms of internal pressure versus molar volume (Fig. 1), each have a maximum. Similar trends for liquid krypton and liquid xenon are reported by Figs. 2 and 3, respectively. Figs. 1–3 also indicate that the volume at the maximum on the isotherms is slightly increasing with increasing temperature. The behavior reported here for argon, krypton, and xenon is also shared by several other liquids for which we had data and we examined.

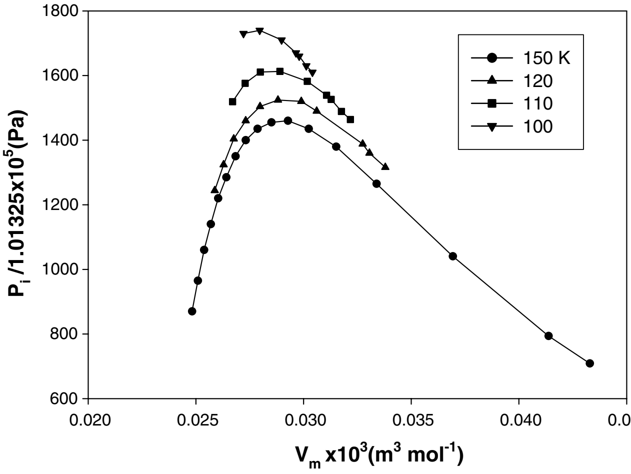

Fig. 1. Internal pressure versus molar volume for liquid argon at different temperature using experimental data [4].

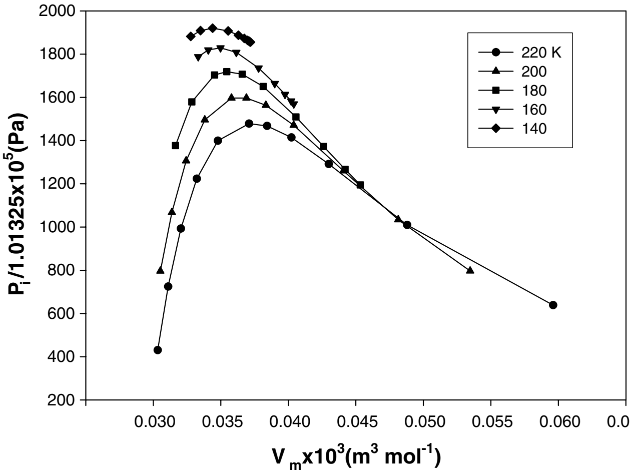

Fig. 2. Internal pressure versus molar volume for liquid krypton at different temperature using experimental data [5].

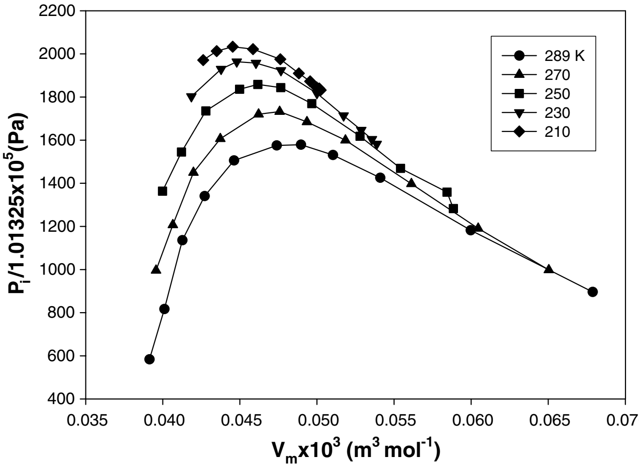

Fig. 3. Internal pressure versus molar volume for liquid xenon at different temperature using experimental data [6].