11th Iranian Physical Chemistry Seminar
University of Mohaghegh Ardabili, July 21-24, 2008

Computation of Some Thermodynamic Properties of He-Kr Mixture Using Molecular Dynamics Simulation

Majid Namayandeh, Elaheh K. Goharshadi, and Mohsen Abbaspour*
Dept. of Chemistry, Ferdowsi University of Mashhad, Mashhad 91779, Iran
majid_namayandeh@yahoo.com

Introduction

In contrast to the large literature on two-body potentials, three-body potentials have been received relatively little attention. Most works reported in the literature have been focused on three-body dispersion as calculated by Axilord and Teller [1]. Wang and Sadus [2] showed there is a simple and accurate relationship between the two-body (U_2) and three-body (U_3) potential energies of a fluid as:

$$U_3 = -\frac{0.85\,\upsilon\rho U_2}{\varepsilon\sigma^6} \qquad (1)$$

where υ is the nonadditive coefficient, $\rho = N/V$ is the number density, ε is the potential well depth, and σ is the distance at which potential becomes zero. U_2 and U_3 stand for two-body and three-body potential, respectively. Hence, the effect of three-body interactions can be incorporated into a simulation involving pair-interactions without any additional computational cost.

The purpose of present work is to form the MD simulation to obtain internal energy, pressure, and diffusion coefficient of He-Kr mixture at wide range of temperatures and densities using molecular dynamics (MD) simulation. We have used (6-12) Lennard-Jones (LJ) potential and HFD-like potential [3] as two-body potentials. We have also incorporated the three-body interactions using the relation proposed by Wang and Sadus [2].

We have also applied the following formula proposed by Smit et al. [4] for calculating the configuration pressure when the total potential (two-body plus three-body interaction potential) is used.

$$P_{conf} = -\left\langle \sum_{i<j}\sum \frac{1}{3V}\frac{dU_2(r_{ij})}{dr_{ij}} r_{ij} \right\rangle + \left\langle \sum_{i<j}\sum \frac{2\nu\rho}{9V\,\varepsilon\sigma^6}\frac{dU_2(r_{ij})}{dr_{ij}} r_{ij} \right\rangle - \left\langle \frac{2\nu\rho^2}{3\varepsilon\sigma^6} U_2 \right\rangle \qquad (2)$$

where

the angle bracket represent ensemble averages.

In order to incorporate the quantum effects, we have also used the FH potential [5] with two-body potentials as:

$$U_{FH}(r) = U_2(r) + \frac{\beta\eta^2}{24\mu}\left[U_2''(r) + 2\frac{U_2'(r)}{r}\right] \qquad (3)$$

where $\beta=1/k_BT$, μ is the reduced mass, and the prime and the double prime are the first and second r derivatives, respectively.

As Eq. (3) shows, the FH potential appears as the sum of the classical two-body, $U_2(r)$ and a quantum correction term that depends on the mass and the temperature.

KEYWORDS Potential energy function; Molecular dynamics simulation; Quantum corrections; Three-Body interactions; Diffusion coefficient

Results

We have performed the MD simulation to obtain internal energy, pressure, and diffusion coefficient of helium-krypton mixtures at different temperatures and densities using Lennard-Jones (LJ) and HFD-like potentials supplemented by quantum corrections following the Feynman-Hibbs approach. The contribution of three-body interactions using an accurate simple relationship reported by Wang and Sadus between two-body and three-body interactions of binary mixtures has been also incorporated in our simulations. Our results for pressure show a very good agreement with the experimental data. Figure 1 shows typical results for the pressure of He-Kr mixture at 298.18 K and x_{He}=0.6. In this figure Q stands for quantum correction. There is a good overall agreement between our simulated values and experiment.

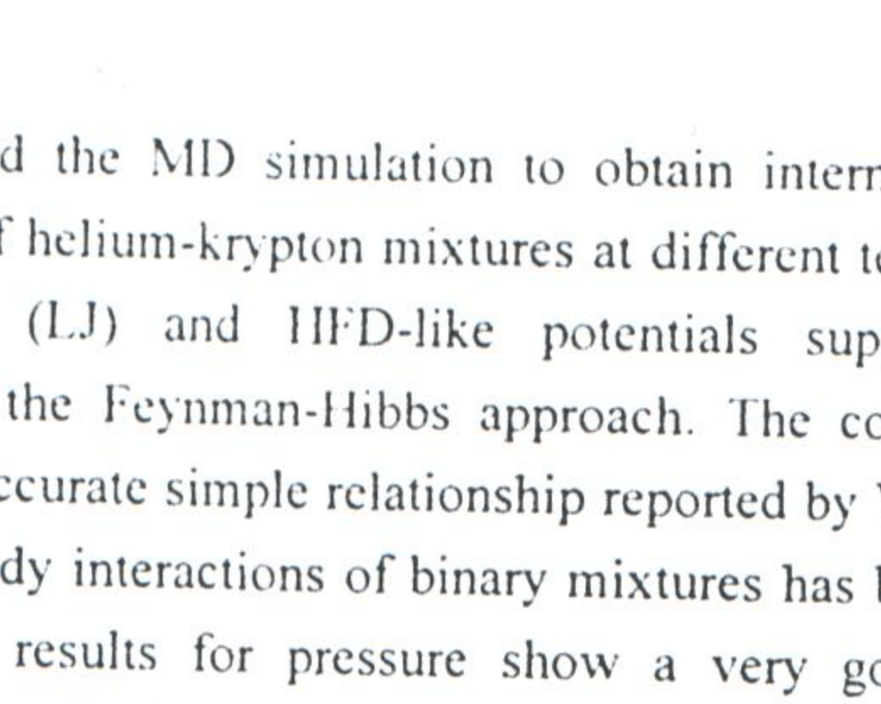

Figure 1. The pressure of He-Kr mixture at 298.15 and x_{He}=0.6

Figure 2 shows the comparison between the simulated results of internal energy at the similar condition of Fig 1. Table 1 shows our results for the diffusion coefficient for He-Kr mixture at 300 K.

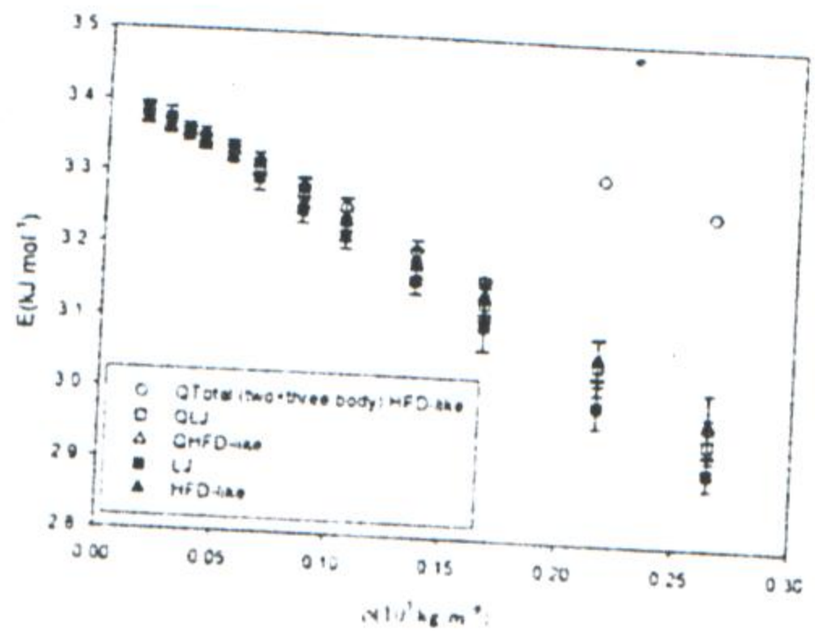

Figure 2. The internal energy of He-Kr mixture at 298.15 and x_{He}=0.6

Table 1. Our calculated values of diffusion coefficients of helium-krypton mixtures using different two-body and total potentials at 300 K

x_{Kr}	P (atm)	D_{exp} (cm^2s^{-1})	D two-body (cm^2s^{-1})				D (total) (cm^2s^{-1})
			LJ	QLJ	HFD-like	QHFD-like	QHFD-like
0.1313	0.8934	0.7115	0.1123	0.1122	0.1123	0.1123	0.1121
0.2100	0.8541	0.7487	0.1377	0.1377	0.1377	0.1377	0.1377
0.3520	0.8806	0.7330	0.2123	0.2123	0.2123	0.2120	0.2120
0.8422	0.8350	0.7815	0.4711	0.4715	0.4713	0.4714	0.4714

References:

1. Axilrod BM, Teller E (1943) J Chem Phys 11: 299
2. Wang L, Sadus RJ (2006) J Chem Phys 125: 144509
3. Goharshadi EK, Moinossadati M (2002) Indian J Chem A 41: 2500
4. Smit B, Hauschild T, Prausnitz M (1992) Mol Phys 77: 1021
5. Feynman RP, Hibbs A (1965) Quantum mechanics and path-integral. McGraw-Hill, New York