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Molecular Dynamics Simulation of Argon, Krypton, and Xenon Using Two-Body and Three-Body Intermolecular Potentials

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Abstract: We have performed the molecular dynamics simulation to obtain energy and pressure of argon, krypton, and xenon at different temperatures using a HFD-like potential which has been obtained with an inversion of viscosity data at zero pressure. The contribution of three-body dispersion resulting from third-order triple-dipole interactions has been computed using an accurate simple relation between two-body and three-body interactions developed by Marcelli and Sadus. Our results indicate that this simple three-body potential which was originally used in conjunction with the BFW potential is also valid when used with the HFD-like potential. This appears to support the conjecture that the relationship is independent of the two-body potential. The energy and pressure obtained are in good overall agreement with the experiment, especially for argon. A comparison of our simulated results with HMSA and ODS integral equations and a molecular simulation have been also included.

1. Introduction

It is well established that the physical properties of fluids are governed overwhelming by interactions involving pairs of molecules. However, the pair-potentials alone are insufficient for qualitatively accurate calculations. To obtain qualitative agreement with experiment, pair-potentials must be used in conjunction with three-body interactions.[1−5]

The practical applications of the three-body interactions are well demonstrated in prediction of the phase-transition of not only pure substances[2−5] but also the three-component mixtures.[6,7] Three-body interactions joined with the mixing rules and an empirical equation of state leads to performance in phase behavior calculations of mixtures.[7]

The important three-body effects have previously remained undetected because earlier works were confined to effective potentials such as Lennard-Jones potential. Even, when regarded simply as effective potentials, the capacity of the pair-potential to reproduce known behavior has its limitation.

The knowledge of interactions in noble gases remains a fundamental question that is not completely solved. Despite the simplicity of their closed-shell electronic structure, it is well-known that a simple pair-potential, through giving the essential features of the structural and thermodynamic properties, is not sufficient for a quantitative description, and many-body effects have to be taken into account.[8]

Molecular simulation is an ideal tool to investigate the role of intermolecular interactions, because, unlike conventional theoretical methods, the contributions from intermolecular potentials can be evaluated rigorously.[9]

Calculations of three-body interactions typically only consider contributions from the Axilrod−Teller[10] (AT) term. The Axilrod−Teller term only accounts for triple-dipole interactions, whereas other three-body interactions arising from high multipoles are possible.

Marcelli and Sadus[3] have shown that vapor−liquid equilibria of argon, krypton, and xenon are affected substantially by three-body interactions. They reported good results for the prediction of the vapor−liquid equilibria of argon, krypton, and xenon using two-body potentials such as the BFW potential[11] plus three-body contributions.

Recently, Jakse et al.[8] performed molecular dynamics simulation to predict thermodynamic properties of liquid krypton using Aziz and Slaman[12,13] plus the triple-dipole Axilrod−Teller potential. It has been shown that the AT potential gives an overall good description of liquid krypton, though other contributions such as higher order three-body dispersion and exchange terms cannot be ignored.

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Table 1. Summary of the Intermolecular Potential Parameters Used in This Work

	argon	krypton	xenon
$(\epsilon/k)/K$	143.224	201.2	282.29
σ/Å	3.3527	3.5709	3.8924
A	99744.4	543237.0	5.54437
α	11.9196	11.0068	−20.1659
β	−2.371328	−3.85189	−24.9602
C_6^*	0.651991	1.57171	7.76621
C_8^*	3.68594	0.580741	−33.5169
C_{10}^*	−2.99307	−0.786392	50.6382
D	1.36	1.37	2.78
ν/(a.u)	518.3[a]	1572.0[a]	5573.0[a]

[a] Reference 19.

Bomont and Bretonent[14] obtained the structural and thermodynamic properties of xenon at supercritical temperature and low densities with the use of an integral equation conjugated with an effective pair potential consisting of the Aziz−Slaman[12,13] two-body potential plus the Axilrod−Teller three-body potential.

The aim of this work is to perform molecular dynamics simulation to obtain internal energy and pressure of argon, krypton, and xenon at different temperatures and densities using a HFD-like potential[15] which has been obtained with an inversion of viscosity data and a simple and accurate expression for computing the three-body dispersion interactions.

2. Theory

2.1. Intermolecular Potential. The prediction of structural and thermodynamic properties of dense fluids requires an accurate knowledge of the intermolecular potential.[14]

In this work, a HFD-like potential[15] which has been obtained from the inversion of the viscosity collision integrals at zero pressure has been used for the pair-interaction potential of argon, krypton, and xenon. It has the following functional form

$$V_2^*(x) = A\exp(-\alpha x + \beta x^2) - f(x)\left(\frac{C_6^*}{x^6} + \frac{C_8^*}{x^8} + \frac{C_{10}^*}{x^{10}}\right) \quad (1)$$

where $f(x)$ is in the form

$$f(x) = \exp\left[-\left(\frac{D}{x} - 1\right)^2\right] \quad x < D \quad (2)$$

$$f(x) = 1 \quad x \geq D \quad (3)$$

where $x = r/\sigma$ and $V_2^* = V_2/\epsilon$ (σ is the distance at which the intermolecular potential has zero value and ϵ is the well depth of potential). The values of parameters σ, ϵ, A, α, β, C_6^*, C_8^*, C_{10}^*, and D have been given in Table 1.

Marcelli and Sadus[16] showed there is a simple and accurate relationship between the two-body (U_2) and three-body (U_3) energies of a fluid

$$U_3 = -\frac{2\nu\rho U_2}{3\epsilon\sigma^6} \quad (4)$$

where ν is the nonadditive coefficient[17] (Table 1), ϵ is the characteristic depth of the pair-potential, σ is the characteristic depth of the pair-potential, and $\rho = N/V$ is the number density obtained by dividing the number of molecules (N) by the volume (V). The significance of this relationship is that it allows us to obtain an accurate overall intermolecular

Table 2. Results of the Reduced Two-Body and Total Pressure of Argon Obtained with the Different Methods

			P_2^*				P_t^*			
T^*	ρ^*	P_{exp}^*[20]	our work	HMSA[21]	MC[22]	MC[3]	our work	HMSA[21]	MC[22]	MC[3]
0.74409	0.73684	0.13062	0.48819			−0.90062	0.57430			−0.53111
0.81850	0.68025	0.04951	0.24982			−0.84150	0.31114			−0.57447
0.83645	0.03262	0.02226	0.02307		0.02800		0.02264		0.46000	
0.84330	0.66634	0.06308	0.23647			−0.81293	0.31923			−0.56658
0.86810	0.65344	0.08202	0.25363			−0.79716	0.27817			−0.56560
0.87827	0.03825	0.02703	0.02765		0.03400		0.02777		0.41100	
0.89291	0.63458	0.08052	0.21168			−0.77647	0.27613			−0.56166
0.91771	0.60873	0.06577	0.16400			−0.73213	0.21702			−0.54491
0.92010	0.59674	0.04373	0.12472		0.05500		0.16301		0.38100	
0.94251	0.59583	0.08933	0.17640			−0.70749	0.21288			−0.53505
0.96192	0.08430	0.05327	0.05607		0.06700		0.05561		0.33700	
0.96731	0.56010	0.07196	0.11881			−0.66315	0.14804			−0.51633
0.99212	0.50942	0.06592	0.07685			−0.58235	0.10680			−0.46706
1.00374	0.10229	0.06440	0.06655		0.08100		0.06599		0.30100	
1.04556	0.12014	0.07633	0.07952		0.09600		0.07807		0.24600	
1.33830	0.85389	0.36709	0.37090	4.36880			0.34751	5.28305		
	0.56926	0.24916	0.25110	0.58050			0.23510	0.80223		
	0.28463	0.13504	0.13660	0.21100			0.12927	0.23541		
1.67290	0.85389	0.56680	0.57440	5.95390			0.53351	6.91950		
	0.56926	0.35948	0.36330	1.18850	0.33541	1.39990				
	0.28463	0.18259	0.18340	0.37470	0.17478	0.39807				

Table 3. Results of the Reduced Two-Body and Total Pressure of Krypton Obtained with the Different Methods

			P_2^*		P_t^*		
T^*	ρ^*	P_{exp}^{*} [20]	our work	MC[3]	our work	MD[8]	MC[3]
0.84000	0.66340	0.10119	−0.53140		−0.44205	0.04248	
	0.64750	0.03296	−0.53300		−0.47418	−0.03526	
0.98910	0.55100	0.11988	−0.23940		−0.19387	0.08134	
	0.53090	0.09135	−0.23290		−0.18868	0.06363	
	0.51500	0.07593	−0.21160		−0.17064	0.04248	
0.75261	0.71073	0.04991	−0.72324	−0.90058	−0.62544		−0.50989
0.82787	0.66980	0.08258	−0.57236	−0.84949	−0.46968		−0.54295
0.85296	0.64087	0.03838	−0.48708	−0.80841	−0.43467		−0.53494
0.87804	0.62988	0.06766	−0.45756	−0.78537	−0.38750		−0.52993
0.90313	0.61489	0.08398	−0.40180	−0.75933	−0.34952		−0.52592
0.92822	0.58397	0.06523	−0.37392	−0.70423	−0.29939		−0.50188
0.95331	0.52707	0.05404	−0.25748	−0.61708	−0.23984		−0.45980
0.97839	0.50809	0.06300	−0.21648	−0.57400	−0.14064		−0.43576

Table 4. Results of the Reduced Two-Body and Total Pressure of Xenon Obtained with the Different Methods

			P_2^*			P_t^*		
T^*	ρ^*	P_{exp}^{*} [20]	our work	ODS[14]	MC[3]	our work	ODS[14]	MC[3]
0.74657	0.70725	0.02117	−1.16729		−0.94452	−0.25177		−0.50168
0.82123	0.67220	0.08986	−0.94928		−0.87271	−0.17600		−0.50966
0.84612	0.63514	0.02745	−0.87358		−0.82583	−0.22573		−0.51266
0.87100	0.61810	0.03380	−0.78728		−0.77696	−0.21519		−0.48972
0.89589	0.60006	0.04757	−0.76306		−0.74904	−0.15933		−0.48972
0.92077	0.57904	0.05781	−0.66313		−0.69418	−0.18678		−0.45979
0.94566	0.51792	0.05464	−0.49508		−0.60940	−0.15966		−0.43187
0.97054	0.51191	0.06372	−0.46026		−0.59444	−0.16077		−0.42588
1.05210	0.01000	0.00900	0.01010	0.00100		0.01004	0.01030	
	0.02000	0.01930	0.01910	0.01000		0.01904	0.01970	
	0.03000	0.02801	0.02710	0.02000		0.02687	0.02816	
	0.04000	0.03634	0.03410	0.03000		0.03363	0.03624	
	0.05000	0.04353	0.04010	0.03300		0.03978	0.04367	
	0.06000	0.05034	0.04530	0.04000		0.04517	0.05051	
	0.07000	0.05640	0.04970	0.05000		0.04858	0.05672	
	0.08000	0.06170	0.05190	0.05500		0.05171	0.06144	
	0.09000	0.06662	0.05560	0.05900		0.05467	0.06734	
	0.10000	0.07116	0.05770	0.06300		0.05629	0.07155	
1.23990	0.10000	0.09538	0.07990	0.04000		0.07833	0.09558	
	0.20000	0.15352	0.08690	0.05000		0.08408	0.15676	
	0.30000	0.20098	0.03300	0.07000		0.03795	0.21107	
	0.40000	0.26798	−0.04650	0.08000		−0.02441	0.28603	
	0.50000	0.42014	−0.10280	0.10000		−0.06368	0.46271	
	0.60000	0.79485	−0.03360	0.28000		0.36258	0.88335	
	0.70000	1.65480	0.35880	0.50000		0.48781	1.91646	
	0.80000	3.47387	1.46250			1.64453		
	0.90000		3.73960			3.97214		
	1.00000		7.96360			8.30149		
1.48780	0.10000	0.12718	0.11020	0.13000		0.11015	0.13305	
	0.20000	0.22710	0.16050	0.14000		0.15539	0.25051	
	0.30000	0.33157	0.17870	0.15000		0.16600	0.35789	
	0.40000	0.48145	0.17870	0.24000		0.17266	0.54145	
	0.50000	0.75700	0.23920	0.37000		0.24185	0.87643	
	0.60000	1.31415	0.47390	1.00000		0.51115	1.54455	
	0.70000	2.43603	1.12640	2.00000		1.20065	2.76233	
	0.80000		2.54350			2.64981		
	0.90000		5.17790			5.43715		
	1.00000		9.73500			10.10352		

Table 5. Results of the Reduced Two-Body and Total Energy of Argon Obtained with the Different Methods

			U_2^*				U_t^*			
T^*	ρ^*	U_{exp}^{*}[20]	our work	HMSA[21]	MC[22]	MC[3]	our work	HMSA[21]	MC[22]	MC[3]
0.74409	0.73684	−3.30527	−3.35367			−4.69269	−3.23940			−4.52502
0.81850	0.68025	−2.81756	−2.86545			−4.29584	−2.77531			−4.16488
0.83645	0.03262	0.95980	1.00584		−4.09025		1.00432		−3.91878	
0.84330	0.66634	−2.68473	−2.73035			−4.12718	−2.64622			−4.00317
0.86810	0.65344	−2.55862	−2.59525			−4.02797	−2.51683			−3.90991
0.87827	0.03825	0.98626	1.02802		−3.88950		1.02620		−3.73392	
0.89291	0.63458	−2.40051	−2.43705			−3.95852	−2.36554			−3.84642
0.91771	0.60873	−2.20584	−2.23684			−3.79979	−2.17387			−3.69760
0.92010	0.59674	−2.13602	−2.16291		−3.69712		−2.10322		−3.55576	
0.94251	0.59583	−2.08309	−2.10637			−3.68073	−2.04833			−3.58450
0.96192	0.08430	0.76634	0.83004		−3.52146		0.82680		−3.40018	
0.96731	0.56010	−1.84071	−1.84373			−3.46247	−1.79598			−3.37516
0.99212	0.50942	−1.56732	−1.52691			−3.16484	−1.49094			−3.08943
1.00374	0.10229	0.71840	0.76757		−3.21198		0.76394		−3.10407	
1.04556	0.12014	0.68109	0.74673		−2.91085		0.74258		−2.83223	
1.33830	0.85389	0.78712	0.80600	−2.71680			0.77417	−1.81477		
	0.56926	1.29048	1.31960	−1.26204			1.28486	−0.91675		
	0.28463	1.82797	1.84520	0.27971			1.82091	0.39347		
1.67290	0.85389	1.47807	1.49490	−1.90376			1.43587	−0.98199		
	0.56926	1.96802	1.98670	−0.61563			1.93440	−0.27268		
	0.28463	2.46931	2.48960	0.90337			2.45683	0.99705		

Table 6. Results of the Reduced Two-Body and Total Energy of Krypton Obtained with the Different Methods

			U_2^*			U_t^*		
T^*	ρ^*	U_{exp}^{*}[20]	our work	MD[8]	MC[3]	our work	MD[8]	MC[3]
0.84000	0.66340	1.26558	−3.18900	−4.12700		−3.06925	−3.93800	
	0.64750	1.35636	−3.10210	−4.03400		−2.98840	−3.85500	
0.98910	0.55100	1.24387	−2.17200	−3.35800		−2.10426	−3.23200	
	0.53090	1.27754	−2.05070	−3.24500		−1.98907	−3.12700	
	0.51500	1.29691	−1.96240	−3.16500		−1.90519	−3.05300	
0.75261	0.71073	0.81780	−3.70726		−4.50562	−3.55811		−4.32198
0.82787	0.66980	1.21665	−3.26815		−4.09419	−3.14424		−3.94167
0.85296	0.64087	1.43220	−3.03006		−3.98381	−2.92014		−3.84232
0.87804	0.62988	1.54769	−2.90028		−3.89350	−2.79687		−3.75903
0.90313	0.61489	1.68417	−2.74915		−3.76304	−2.65346		−3.63661
0.92822	0.58397	1.90491	−2.50161		−3.56235	−2.41892		−3.44695
0.95331	0.52707	2.15395	−2.16448		−3.24124	−2.09990		−3.14290
0.97839	0.50809	2.36644	−4.96536		−3.11079	−4.82255		−3.02047

potential (V) solely in terms of pair contributions (V_2) and well-known intermolecular parameters:

$$V = V_2\left(1 - \frac{2\nu\rho}{3\epsilon\sigma^6}\right) \tag{5}$$

Therefore, the effect of three-body interactions can be incorporated into a simulation involving pair-interactions without any additional computational cost.[4] Comparison of this approach with a full two-body plus three-body calculation indicates that there is no significant loss of accuracy.[16] In this work, we have used this equation in our simulations.

2.2. Simulation Details. The molecular dynamics simulations for 1000 atoms of argon, krypton, and xenon have been performed. The simulations were performed in cubic boxes, and the conventional periodic boundary conditions were applied. The NVT ensemble was implemented using a Nose-Hoover thermostat for the systems of argon, krypton, and xenon interacting via the two-body HFD-like (eqs 1−3) and then via the overall intermolecular potential (eq 5). Before including the three-body interactions, simulations were performed with the two-body part of the potential only for the same thermodynamic states as those intended for the overall intermolecular potential. The number of time steps, n_t, size of time steps, Δt^*, and the cutoff radius, r_c, have been chosen as 5000, 0.001, and 2.5σ, respectively. The long-range correction terms were evaluated to recover the contribution to the pressure and energy for the intermolecular potential.

3. Results and Discussion

We have used the HFD-like potential (eqs 1−3) in the MD simulations for two-body intermolecular potentials of argon,

Table 7. Results of the Reduced Two-Body and Total Energy of Xenon Obtained with the Different Methods

			U_2^*			U_t^*		
T^*	ρ^*	U_{exp}^{*} [20]	our work	ODS[14]	MC[3]	our work	ODS[14]	MC[3]
0.74657	0.70725	0.87782	−2.14716		−4.45953	−2.04718		−4.25148
0.82123	0.67220	1.24190	−1.92124		−4.08126	−1.83621		−3.90109
0.84612	0.63514	1.48500	−1.76169		−3.91204	−1.68802		−3.74779
0.87100	0.61810	1.64544	−1.67746		−3.78263	−1.60919		−3.62834
0.89589	0.60006	1.79626	−1.58138		−3.62337	−1.51890		−3.47903
0.92077	0.57904	1.96118	−1.48350		−3.51387	−1.42694		−3.37949
0.94566	0.51792	2.19060	−1.24671		−3.15551	−1.20420		−3.04203
0.97054	0.51191	2.40642	−1.21201		−3.11570	−1.17116		−3.00719
1.05210	0.01000	5.44816	1.50190	−0.36650		1.50091	−0.46651	
	0.02000	5.37399	1.42320	−0.42250		1.42133	−0.52249	
	0.03000	5.30024	1.33230	−0.05000		1.32967	−0.14720	
	0.04000	5.22437	1.22860	−0.55000		1.22536	−0.65047	
	0.05000	5.15275	1.14650	−0.61000		1.14273	−0.71844	
	0.06000	5.07943	1.06350	−0.68000		1.05930	−0.78641	
	0.07000	5.00782	0.99730	−0.74000		0.99270	−0.84641	
	0.08000	4.93962	0.88370	−0.81000		0.87905	−0.91039	
	0.09000	4.87013	0.82360	−0.87000		0.81872	−0.97038	
	0.10000	4.79980	0.74890	−0.90000		0.74397	−0.99950	
1.23990	0.10000	5.15275	1.05940	−1.07000		1.05242	−1.07338	
	0.20000	4.56279	0.32560	−1.53000		0.32131	−1.57375	
	0.30000	4.03085	−0.42490	−2.00000		−0.41651	−2.04602	
	0.40000	3.53723	−1.06000	−2.30000		−1.03208	−2.49943	
	0.50000	3.03176	−1.75150	−2.83000		−1.69384	−2.93400	
	0.60000	2.51563	−2.43680	−3.20000		−2.34054	−3.38742	
	0.70000	2.01664	−3.15350	−3.64000		−3.00816	−3.84084	
	0.80000	1.58713	−3.81620	−3.90000		−3.61519	−4.18155	
	0.90000		−4.36070	−4.00000		−4.10230	−4.40014	
	1.00000		−4.67150	−3.90000		−4.36393	−4.39332	
1.48780	0.10000	5.57050	1.48780	−1.11000		1.47800	−1.11870	
	0.20000	5.02231	0.78660	−1.60000		0.77624	−1.60641	
	0.30000	4.50653	0.09110	−1.92000		0.08930	−2.02687	
	0.40000	4.00890	−0.58080	−2.35000		−0.56550	−2.48081	
	0.50000	3.51097	−1.26400	−2.70000		−1.22239	−2.90083	
	0.60000	3.01390	−1.95530	−3.10000		−1.87806	−3.32099	
	0.70000	2.54590	−2.62940	−3.40000		−2.50822	−3.70738	
	0.80000		−3.24110	−3.50000		−3.07038	−4.03723	
	0.90000		−3.72600	−3.60000		−3.50521	−4.19822	
	1.00000		−3.98720	−3.20000		−3.72468	−4.14406	

krypton, and xenon. The total (two-body plus three-body) contributions have been considered in the simulation using eq 5.

Our results of reduced pressure and energy for argon, krypton, and xenon in the NVT ensemble have been compared at different temperatures and densities with experimental and previous theoretical works in Tables 2−7. We have also considered the corrections to calculation of pressure using the total intermolecular potential (eq 5) proposed by Smit et al.[18] The normal conventions have been adopted for the reduced density ($\rho^* = \rho\sigma^3$), reduced temperature ($T^* = kT/\epsilon$), reduced energy ($U^* = U/\epsilon$), and reduced pressure ($P^* = P\sigma^3/\epsilon$). In Tables 2−7, the subscripts 2 and t denote two-body, three-body, and two-body plus three-body contributions, respectively.

Three-body interactions based on the triple-dipole dispersion term of Axilrod and Teller contribute commonly 5−10% to the overall energy of the liquid phase. The data in Tables 5−7 indicate that the three-body interactions via the expression of Marcelli and Sadus[16] contribute to the total energy of argon, krypton, and xenon 0.15−4.11%, 2.96−4.19%, and 0.13−7.05%, respectively.

As Tables 2−7 show the contribution of the three-body interaction on pressure and energy based on the Marcelli and Sadus expression is almost the same contribution as the three-body interaction using the Axilrod−Teller expression. A situation such as this has been obtained by Marcelli and Sadus.[16,19] They performed the nonequilibrium molecular dynamics (NEMD) for argon and found that the calculations of energy and pressure (by concerning the Smit et al.[18] corrections) using eq 5 were in good agreement with the two-body (BFW potential) + three-body (Axilrod-Teller potential) energy and pressure. They have also used the Smit et al.[18] correction to calculation of pressure using eq 5.

As Table 2 shows there is a better accordance between our simulated values of two-body and total pressure of argon

and the experimental values[20] than other simulation and theories.[3,21,22] This agreement may be mainly due to the two-body potential of argon used in our calculations because the agreement with the experiment for the two-body pressure is better than total pressure.

Our results of two-body and total pressure of argon are better than that of an integral equation theory (HMSA)[21] which has used the two-body potential of Aziz and Slaman[12,13] and the three-body potential of Axilrod-Teller. Our simulation is also better than those calculated using Monte Carlo (MC) simulations of Sadus and Prausnitz[22] and Marcelli and Sadus[3] which have used the two-body Lennard-Jones and BFW[11] potentials, respectively. These two preceding works have used the Axilrod−Teller expression for three-body simulations.

Table 3 shows that our calculated two-body pressures are larger than those obtained using MC simulations[3] but are smaller than the experimental values.[20] The same situation occurs for the total pressure of krypton. It is shown that our results of total pressure have more accordance with experimental values than two-body pressure values, and this is due to considering the three-body contribution of Marcelli and Sadus in our calculation. We have also compared our results with the molecular dynamics (MD) simulation of Jakse et al.[8] which have used the HFD potential of Aziz and Slaman[12,13] in conjunction with the three-body interactions relation of Axilrod−Teller. The MD results of Jakse et al.[8] have good agreement with the experiment but our results underestimate the experimental values, and it can be referred to as the kind of two-body potential of krypton which has been used in the calculations.

We have compared our calculated reduced two-body and the two-body plus three-body pressure of xenon with the experiment[20] in Table 4. The results of the MC simulation of Marcelli and Sadus[3] and an integral equation theory (ODS)[14] which has used the HFD potential of Aziz and Slaman[12,13] in conjunction with the three-body interactions of Axilrod−Teller have been also considered for this comparison. It is clear that our results are in a fairly good agreement with the experiment. It is shown that the three-body interactions have affected the total pressure of xenon especially at higher densities. Our results are also better than those obtained using MC simulations, but the results of the ODS theory are better than our calculations at some points.

It is evident from Table 5 that there is a very good accordance between our simulated values of two-body and the total energy of argon and the experimental values.[16] Our results are also better than those calculated using the HMSA theory[21] and the MC simulations.[3,22] The reason for our good results for argon is due to our two-body potential with the three-body term of Marcelli and Sadus used in the calculations because the three-body term has improved our results in this table.

We have compared our reduced two-body and the total energy of krypton and xenon with the experiment[20] and the other theories and simulations[3,10,14] in Tables 6 and 7. It is obvious that our results underestimate the experimental values but much better than other previous works, and this may be attributed to the use of more accurate pair-potential for these compounds.

4. Concluding Remarks

We have performed the molecular dynamics simulation to obtain energy and pressure of argon, krypton, and xenon at different temperatures and densities using a two-body HFD-like potential which has been obtained with an inversion of viscosity data at zero pressure, and the three-body interactions have been calculated using the Marcelli and Sadus expression.

The energy and pressure obtained are in good overall agreement with the experiment, especially for argon, and this can be due to the two-body potential used in this work. A comparison of our simulated results with the corresponding values obtained from HMSA and ODS integral equations and molecular simulation is also included.

Our results indicate that the simple three-body potential of Marcelli and Sadus which was originally used in conjunction with the BFW potential is also valid when used with the HFD-like potential. This appears to support the conjecture that the relationship is independent of the two-body potential.

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