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Research note

The Modified Lennard-Jones and Devonshire Equation of State

F. Aghamiri[*1], *H. Modarress*[2], *G. A. Mansoori*[3]

1- Department of Chemical Engineering, University of Isfahan, Isfahan, Iran
2- Department of Chemical Engineering, Amir-Kabir University of Technology, Tehran,Iran
3- Department of Chemical Engineering, University of Illinois at Chicago, Chicago, USA

Abstract

Lennard-Jones-Devonshire equation of state is an old but theoretical based EOS. The concept of the nearest neighboring molecules or coordination number is proposed to be a function of temperature and volume, whereas it is a constant in the original. The dilute gas and hard sphere limits of molecules are employed to determine this function. Improvement of this modification is demonstrated by property calculations for Lennard-Jones fluid. Results of the modified LJD equation of state offer senior accord with simulation data of Lennard-Jones fluid than those of the original version.

Keywords: *Lennard-Jones Fluid, Lennard-Jones Devonshire theory, Equation of state, Hard spheres, Nearest neighboring molecules*

1- Introduction

A liquid or a dense gas may be regarded either as a very imperfect gas in which multiple collisions are frequent (gas-like approach) or as a distorted crystal in which the long-range order has been lost (crystal-like approach) [1]. A good example of the gas-like approach is virial theory, that is at present of no value in making practical numerical calculations in high-density region, because of possible difficulties in convergence in the liquid range [1].

There are two main types of crystal-like approaches: (i) cell theories, in which a liquid is regarded as a distorted crystal with no molecule located at or near each lattice point, and (ii) hole theories, in which it is realized that liquids differ from crystals in that, some lattice sites are vacant [2].

Lennard-Jones and Devonshire (LJD) equation of state belongs to a general class of cell theories [3]. In this theory, a liquid is treated like a solid in which molecules no longer vibrate harmonically about their lattice sites, but are allowed to wander throughout a space bounded by their neighboring molecules. A number of modifications have been proposed in order to improve agreement of results of LJD theory with experimental data [1,4]. This theory has also been modified to predict solid-liquid and liquid-vapor phases transitions, simultaneously [4-5]. LJD equation of state has been used to calculate solid free energy in order to predict solid-liquid equilibrium [6]. According to Sadr-Lahijany et al [7] there is evidence for a liquid-liquid phase transition found using a LJD-like cell theory. Configurational properties of water clathrates are studied using mont carlo and multidimensional

* Corresponding author: E-mail: aghamiri@petr.ui.ac.ir

integration and compared with LJD theory [8].

LJD theory has been used to obtain an equation-of-state (EOS) for chain molecular systems. Interactions of the central segment with second and third shells of neighbors are taken into account. Application of this theory to polymer glasses of diverse structures is found to be quite successful in explaining PVT behavior over a wide range of temperatures both at atmospheric and elevated pressures [9]. The cell theory of LJD has been re-analysed and it has been shown that, in addition to critical point originally reported for 12-6 potential, model exhibits a further critical point. The latter has been introduced as a more appropriate liquid-gas critical point [10]. Recently Anderson investigated an application of Lennard-Jones and Devonshire theory for consideration of intermolecular potential between guest molecules and host molecules for hydrates formation in which Langmuir constants can be computed, either using experimental data or from *ab initio* data. This method was used to predict existing mixed hydrate phase equilibrium data without any fitting parameters [11].

2- Theory

According to LJD theory, N rigid spheres occupy a total volume V and are arranged in form of a face-centered cubic lattice. Each molecule in the lattice has twelve nearest neighbors, where the distance between two neighboring molecules is presented by a. The cell corresponding to this volume is dodecahedral [1, 4-5], and each molecule is wandering in its cage or cell formed by its nearest neighbors. The nearest neighbors occupy midpoints of twelve edges of an imaginary cube constructed about any given molecule. The volume per molecule, $v = V/N$, is related to distance between nearest neighbors as follows:

$$v = a^3/\sqrt{2} \qquad (1)$$

According to original LJD theory, the wanderer molecule has interaction with its nearest neighbors. Under such conditions free volume , v_f, is just that volume available to center of the wandering molecule. Molecular partition function of LJD theory is given by the following equation [1, 3, and 5]:

$$Q = exp(-N\,\varphi(0)/2kT)\,[(2\pi m\,kT/h^2)^{3/2}\,v_f\,e)]^N \qquad (2)$$

where N is number of molecules, T is absolute temperature, m is mass of molecule, h is Plank's constant, v_f is free volume, and finally $exp(-N\varphi(0)/2kT)$ is considered interaction between all atoms when stay on their lattice occupation position with respect to a zero energy level, in which distance between all N atoms is infinity. $\varphi(0)$ is obtained by using Lennard-Jones (6–12) pair potential function (L-J (6–12)) [4]. Also by integrating L-J (6–12) pair potential function over all angels between a central molecule and its nearest neighbors, v_f can be calculated [1, 5, 10, 11]. By using v_f and $\varphi(0)$ in equation (2) and upon substituting for the partition function, Q, in equation (3):

$$P=kT(\partial\, lnQ/\partial\, V)_T \qquad (3)$$

LJD equation of state is obtained as the following form:

$$Z=1+[2C/T^*][(1+2g_l/g)v^{*-4}-(1+2g_m/g)v^{*-2}] \qquad (4)$$

where C is number of first nearest neighboring molecules that is equal to 12 for a face-centered cubic lattice. Terms of $T^*=kT/\varepsilon$ and $v^*=v/\sigma^3$ are reduced temperature and specific volume, respectively, where ε and σ are energy and size parameters of LJ potential function [4]. In equation (4) g, g_l and g_m are given by the following integrals:

$$g = \int_0^{y_0} y^{1/2} \exp[-(C/T^*)(l(y)v^{*-4} - 2\, m(y)v^{*-2})]dy \quad (5)$$

$$g_l = \int_0^{y_0} y^{1/2} \exp[-(C/T^*)(l(y)v^{*-4} - 2\, m(y)v^{*-2})]l(y)dy \quad (6)$$

$$g_m = \int_0^{y_0} y^{1/2} \exp[-(C/T^*)(l(y)v^{*-4} - 2\, m(y)v^{*-2})]m(y)dy \quad (7)$$

where

$$l(y) = (1+12y+25.2y^2+12y^3+y^4)(1-y)^{-10}-1 \quad (8)$$

$$m(y) = (1+y)(1-y)^{-4}-1 \quad (9)$$

$$y = r^2/a^2 \quad (10)$$

LJD equation of state, Equation (4), can also be presented in another form when interaction of the wanderer molecule with the first three neighboring shells of molecules is considered [1]:

$$Z = 1+(2C/T^*)[(1.011+2\,G_l/G)v^{*-4} - (1.2045+2\,G_m/G)v^{*-2}] \quad (11)$$

In a face-centered cubic lattice, the first shell of neighbors has 12 molecules at distance a, the second shell has 6 molecules at a distance $a\sqrt{2}$, and the third shell has 24 molecules at a distance $a\sqrt{3}$. In Equation (11), functions G, G_l, G_m are integrals like those of g, g_l, g_m respectively, except functions $l(y)$ and $m(y)$ are replaced by functions $L(y)$ and $M(y)$ respectively as:

$$L(y)=l(y)+(1/128)l(y/2)+(1/729)l(y/3) \quad (12)$$

$$M(y)=m(y)+(1/16)m(y/2)+(2/27)m(y/3) \quad (13)$$

where $l(y)$ and $m(y)$ are given by Equations (8) and (9) respectively.

3- Modification of Lennard – Jones - Devonshire theory

The two crucial tests for a derived theoretical equation of state are its ability to meet both dilute gas and high temperature (hard sphere) limits [12-13]. The former limit is usually investigated by the second virial coefficient [13], whereas the latter limit is examined by comparing equation of state with the Carnahan-Starling equation of state [14].

The second virial coefficient, B_2, can be obtained by using the compressibility coefficient Z, through the following relation [13]:

$$B_2 = \lim_{V\to\infty}[(Z-1)V] \quad (14)$$

According to equation (4) second virial coefficient, B_2, is equal to zero [1]. Also compressibility factor Z given by Equation (4), approaches unity in a limit of high temperature ($T \to \infty$). These results show the shortcomings of LJD equation of state in these limits, and can be attributed to assumptions made in this theory. In this theory number of nearest neighboring molecules is considered as a constant. This is a characteristic of lattice type that applied for determining the molecular arrangement. Although, for solids this can be a reasonable assumption, in the case of liquids and gases it can not be accepted. It is a well-known fact that coordination number or number of nearest neighboring molecules in liquids and dense gases is generally a function of temperature and density [15].

In this work the following general temperature and volume functionality for coordination number C is introduced:

$$C = C(T^*, v^*) \quad (15)$$

By using Equation (15) new expressions for

v_f and $\varphi(0)$ are easily derived and substituted in Equation (2) to obtain a new partition function of LJD theory. Then by differentiating new partition function with respect to V at constant temperature the modified LJD compressibility factor will be obtained as:

$$Z=Z_{LJD} - 0.5\,(\partial C/\partial v)_T\,(V/T^*)[v^{*-4}(1+2g_l/g) - 2v^{*-2}(1+2g_m/g)] \quad (16)$$

Where Z_{LJD} has the same form given by Equation (4) in which C is a function of temperature and volume. It is worth noting that Equation (16) is obtained for the case that the effect of the first shell of neighboring molecules is considered. A similar relation can be obtained when the effect of the first three shells of neighboring molecules is considered. It should be pointed out that a number of various functions for C can be proposed in which the second virial coefficient and (or) high temperature limits of *LJD EOS* are existed. However any proposed function for C, has to satisfy the following conditions:

$$\lim_{v^*\to\infty}(C/v^*) = finite \quad (17)$$

$$\lim_{T^*\to\infty}(C/T^*) = finite \quad (18)$$

$$\lim_{v^*\to v^*_{cp}}(C) = C_o \quad (19)$$

Where v_{cp} is proposed as reduced closed pack volume of cells, and C_o is the coordination number in closed pack volume, both are the characteristics of the lattice model structure. For example v^*_{cp} and C_o are equal to $1/\sqrt{2}$ and 12, respectively, in a face-centered cubic lattice. The above conditions can guide us to the convenient functions for coordination number.

Therefore the simplest expression for C that can satisfy conditions (17)-(19) is proposed as follows:

$$C = C_o + \left(\frac{a_o}{T^*} + a_1T^*\right)(v^*-v^*_{cp}) + a_2T^*\left(\frac{1}{v^*} - \frac{1}{v^*_{cp}}\right) \quad (20)$$

where a_o, a_1, and a_2 are adjustable parameters, which their values obtained by calculations.

Now, one can substitute equation (20) in equation (16) in order to obtain a new version of LJD equation of state, as:

$$Z = 1 + \left[\frac{2}{T^*}\left(C_o + \frac{a_o}{T^*} + a_1T^*\right)(v^*-v^*_{cp}) + a_2T^*\left(\frac{1}{v^*} - \frac{1}{v_{cp}}\right)\right]\left[(1+2g_l/g)v^{*-4} - (1+2g_m/g)v^{*-2}\right] -$$

$$0.5\left[\left(\frac{a_o}{T^{*2}} + a_1\right)v^* - \frac{a_2}{v^*}\right]\left[v^{*-4}(1+2g_l/g) - 2v^{*-2}(1+2g_m/g)\right] \quad (21)$$

When the interaction of the wanderer molecule with the first three neighboring shells of molecules is considered:

$$Z=1+\left[\frac{2}{T^*}\left(C_o+\frac{a_o}{T^*}+a_1T^*\right)(v^*-v_{cp}) + a_2T^*\left(\frac{1}{v^*} - \frac{1}{v_{cp}}\right)\right]\left[(1.011+2G_l/G)v^{*-4} - (1.2045 + 2G_m/G)\right.$$

$$\left.v^{*-2}\right] - 0.5\left[\left(\frac{a_o}{T^{*2}} + a_1\right)v^* - \frac{a_2}{v^*}\right]\left[v^{*-4}(1.011+2G_l/G) - 2v^{-2}(1.2045+2G_m/G)\right] \quad (22)$$

It is worth noting that two parameters among three parameters a_o, a_1 and a_2 in Equation (20) may be found using the following conditions:

$$(\partial P/\partial V)_{Tc} = (\partial^2 P/\partial V^2)_{Tc} = 0 \quad (23)$$

Integrals g, g_l, and g_m are functions of the coordination number C, as well as state variables T and V. Also these integrals must be solved numerically. Due to the mathematical complexity it is too difficult to apply conditions of equation (23) on equations (21) or (22). As an alternative method, a_o, a_1 and a_2, may be obtained by correlating equation (21) to simulation data of Lennard-Jones fluid [12].

Application of presented theory can be demonstrated by property calculations as well as study the second virial coefficient and high temperature limits.

An expression for internal energy, U, based on equation (21) is given by the following equation:

$$\frac{U-U^{ig}}{NkT} = -0.5\left[\left(\frac{-a_o}{T^*}+a_1T^*\right)(v^*-v^*_{cp})+a_2T^*\left(\frac{1}{v^*}-\frac{1}{v^*_{cp}}\right)\right]\left[v^{*4}(1+2g_l/g)-2v^2(1+2g_m/g)\right] \quad (24)$$

where U^{ig} is internal energy of ideal gas limit. Similarly when the interaction of the wanderer molecule with the first three neighboring shells of molecules is considered, we get the following expression for internal energy based on equation (22):

$$\frac{U-U^{ig}}{NkT} = -0.5\left[\left(\frac{-a_o}{T^*}+a_1T^*\right)(v^*-v^*_{cp})+a_2T^*\left(\frac{1}{v^*}-\frac{1}{v^*_{cp}}\right)\right]\left[v^{*4}(1.011+2G_l/G)-2v^{*2}(1.0245+2G_m/G)\right] \quad (25)$$

The limit of dilute gas can also be considered by the second virial coefficient. As it was shown earlier, in original LJD equation of state second virial coefficient is equal to zero. However the above mentioned limit can be obtained by the modified LJD theory (equation 22), as the follows:

$$B_2/\sigma^3 = \lim_{v\to\infty}[(Z-1)V] = -4.964(a_oT^{*-2}+a_1) \quad (26)$$

Also presented theory is applied to study high temperature limit. This limit can also be considered as hard sphere limit of molecules. According to original LJD, compressibility factor Z approaches unity in limit of high temperature ($T\to\infty$). This limit can be predicted by modified LJD theory (equation 22), as the follows:

$$\lim_{T\to\infty} Z = Z^{hs} = 1+2a_2[v^{*-1}-v^{*-1}_{cp}+0.25v^{*-1}](1.011+2G^{hs}_l/G^{hs})v^{*-4}-2a_2[v^{*-1}-(v/\sigma^3)^{-1}_{cp}+0.5v^{*-1}](1.2045+2G^{hs}_m/G^{hs})\,v^{*-2} \quad (27)$$

In Equation (27) superscript *hs* indicates the limit for T goes to infinity. It should be noted that Z is equal unity where C is a constant according to original LJD theory.

The above mentioned limits can be calculated provided parameters of equation 20 are available.

Calculations:

Performance of the proposed modification can be demonstrated by comparison of results of modified LJD and original LJD equation of state with simulation data of LJ fluid. In this work internal energy and compressibility factor are chosen to comparison. Available simulation data for Z and U of LJ fluid are those of Verlet (1967) [16]. Extensive calculations indicate that the three-shell modification improves results of LJD theory [1]. Therefore we use the three shell modification expressions for compressibility factor and internal energy, given by equations (22) and (25), respectively. Table 1 represents results of compressibility factor Z, and internal energy U, for modified this work and original LJD theory. Also, reported in this table are simulation data [16] for LJ fluid. In order to obtain results of table 1 for modified LJD we need to have in hand a_o, a_1, and a_2 parameters of equation (20), which can be obtained by minimization of the following function:

$$\Delta=\Sigma_i\{[(Z_{si}-Z_{ci})/Z_{si}]^2+[(U_{si}-U_{ci})/U_{si}]^2\} \qquad (28)$$

where subscript s and c represent simulation data and calculated values, respectively. Summation in equation (28) is extended over all data points. The following results are obtained for parameters of equation (20):

$$a_o=1.27021; \quad a_1=-2.77872; \quad a_2=-6.17568$$

According to Table 1, modified LJD shows a superior agreement with simulation data especially for Z, rather than original LJD. In the above calculations it is assumed that relations between numbers of neighboring molecules of the first three shells are as given by the face-centered cubic lattice model. In this lattice model first shell has 12, the second one has 6 and the third has 24 neighboring molecules. Thus, provided number of molecules in the first neighboring shell is C, these values for second and the third shells are $C/2$ and $2C$, respectively.

The variation of C with reduced temperature and volume is presented by Figure (1) for four different values of (v/v_{cp}) versus reduced temperature T^*. According to this figure coordination number is increased with temperature at constant density. The same result will be obtained when density is reduced at constant T^*. Both results are emphasized on the behavior that is expected for the variable coordination number concept in this work.

Figure 2 shows reduced second virial coefficient (B_2^*) given by equation (26) versus reduced temperature (T^*). Also reported in this figure is B_2^* according to original LJD, which is equal to zero for all temperature.

In Figure 3 compressibility factor (Z) versus v^* at high temperature limit (hard sphere) is presented for modified (equation 27) and original LJD.

In Figures 2 and 3 reduced second virial coefficient and compressibility factor at high temperature limit are equal to zero for original LJD, which it means that this theory can not exhibit good representation at dilute gas and high temperature (hard sphere) limits. They are reasons for short comings of LJD.

4- Conclusion

A temperature and volume dependence function was proposed for coordination number of LJD equation of state. Simulation data of Lennard-Jones fluid were used to determine this function. The modified equation of state could predict second virial coefficient and hard sphere limits, whereas original equation of state failed to predict these limits. In spite of the simplicity of this modification, results were in acceptable agreement with simulation data. The study of coordination number around the critical point will be dealt with in a future work.

Table 1 Compressibility factor Z, and reduced internal energy $(U-U^{ig})/NKT$ as a function of reduced temperature T^* and reduced density ρ^*

ρ^*	T^*	Z			$(U-U^{ig})/NKT$		
		Simulation data [16]	**Original LJD**	**Modified LJD**	**Simulation data**	**Original LJD**	**Modified LJD**
0.88	1.095	3.48	0.74	3.20201	-5.66	-5.82	-5.45
0.88	0.94	2.72	-0.14	2.62580	-5.84	-6.91	-6.45
0.88	0.591	-0.18	-4.72	-0.15541	-6.53	-1163	-10.48
0.85	2.889	4.36	3.54	4.49577	-4.25	-1.63	-1.47
0.85	2.202	4.2	3.07	4.36076	-4.76	-2.37	-2.22
0.85	1.214	3.06	0.82	2.88252	-5.6	-5.00	-4.73
0.85	1.1	2.78	0.43	2.58870	-5.69	-5.44	-5.15
0.85	0.8	1.64	-1.12	1.47378	-5.94	-7.20	-6.77
0.85	0.782	0.98	-2.02	0.86289	-6.04	-8.21	-7.67
0.85	0.786	0.99	-1.97	0.89076	-6.05	-8.16	-7.63
0.85	0.760	0.78	-2.26	0.70413	-6.07	-8.47	-7.90
0.85	0.719	0.36	-2.76	0.38045	-6.12	-9.00	-8.37
0.85	0.658	-0.2	-3.66	-0.18577	-6.19	-9.92	-9.17
0.85	0.591	-1.2	-4.95	-0.96889	-6.26	-11.16	-10.26
0.75	2.849	3.1	2.86	3.32843	-4.07	-1.48	-1.44
0.7	1.304	1.61	0.69	1.73244	-5.02	-3.97	-3.91
0.7	1.069	0.9	-0.34	0.90674	-5.19	-4.99	-4.91
0.75	1.071	0.89	-0.33	0.91578	-5.17	-4.98	-4.89
0.75	0.881	-0.12	-1.69	-0.17687	-5.31	-6.22	-6.09
0.75	0.827	-0.54	-2.22	-0.59649	-5.38	-6.68	-6.53
0.65	2.557	2.14	2.28	2.36483	-3.78	-1.48	-1.52
0.65	1.585	1.25	1.23	1.46992	-4.23	-2.68	-2.74
0.65	1.036	-0.11	-0.57	-0.11940	-4.52	-4.38	-4.50
0.65	0.9	-0.74	-1.38	-0.82152	-4.61	-5.12	-5.27
0.55	2.645	1.63	2.06	1.81990	-3.24	-1.18	-1.27
0.5426	3.26	1.86	2.25	1.97412	-3.0	-0.88	-0.96
0.5426	1.404	0.57	0.81	0.62049	-3.63	-2.53	-2.72
0.5426	1.326	0.42	0.65	0.46327	-3.66	-2.70	-2.91
0.5	1.36	3.4	0.79	0.46043	-3.38	-2.40	-2.64

Table 1. (*Continue)*

ρ^*	T^*	Z			$(U-U^{ig})/NKT$		
		Simulation data	**Original LJD**	**Modified LJD**	**Simulation data**	**Original LJD**	**Modified LJD**
0.45	4.625	1.68	2.19	1.78722	-2.22	-0.43	-0.54
0.45	2.935	1.38	1.92	1.51738	-2.6	-0.84	-0.96
0.45	1.744	0.74	1.28	0.86734	-2.9	-1.62	-1.81
0.45	1.764	0.76	1.3	0.88657	-2.89	-1.59	-1.79
0.85	1.71	0.74	1.25	0.83354	-2.95	-1.65	-1.86
0.85	1.552	0.75	1.07	0.65548	-2.98	-1.85	-2.09
0.85	1.462	0.41	0.97	0.45428	-2.72	-1.76	-2.07
0.85	1.424	0.38	0.93	0.39971	-2.73	-1.81	-2.14
0.85	1.62	0.58	1.12	0.57596	-2.31	-1.37	-1.67
0.75	1.418	0.4	0.92	0.34124	-2.21	-1.6	-1.97
APE%			**9152**	**2.87**		**7.4**	**6.19**

$$APE\% = \frac{100}{n_d}\sum\sqrt{\left(\frac{M_{sim}-M_{cal}}{M_{sim}}\right)^2}$$

n_d is number of data point, M is property and subscripts sim and cal are simulation data and calculated, respectively.

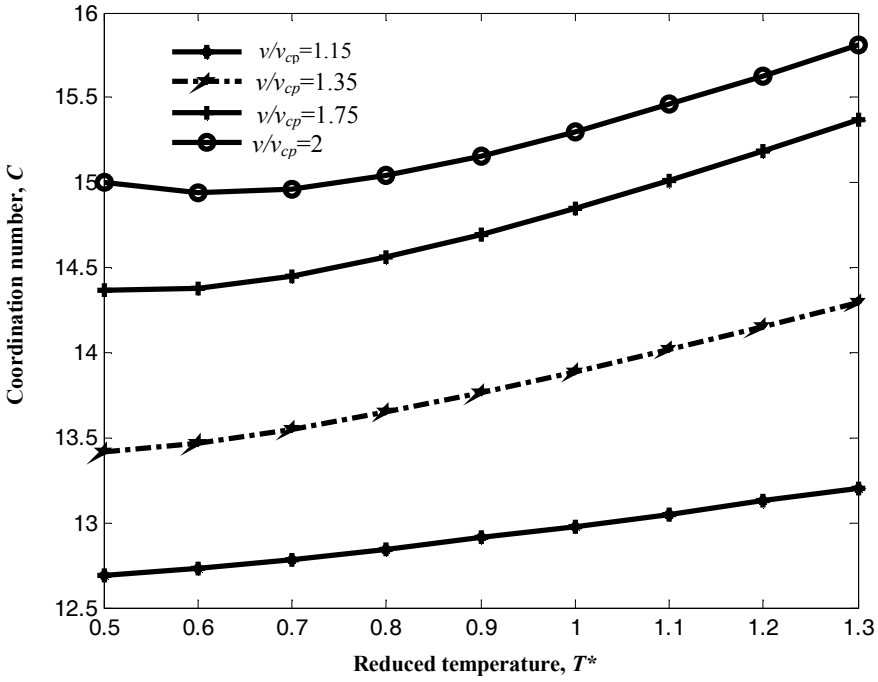

Figure 1. Coordination number C versus T^* for different reduced volumes.

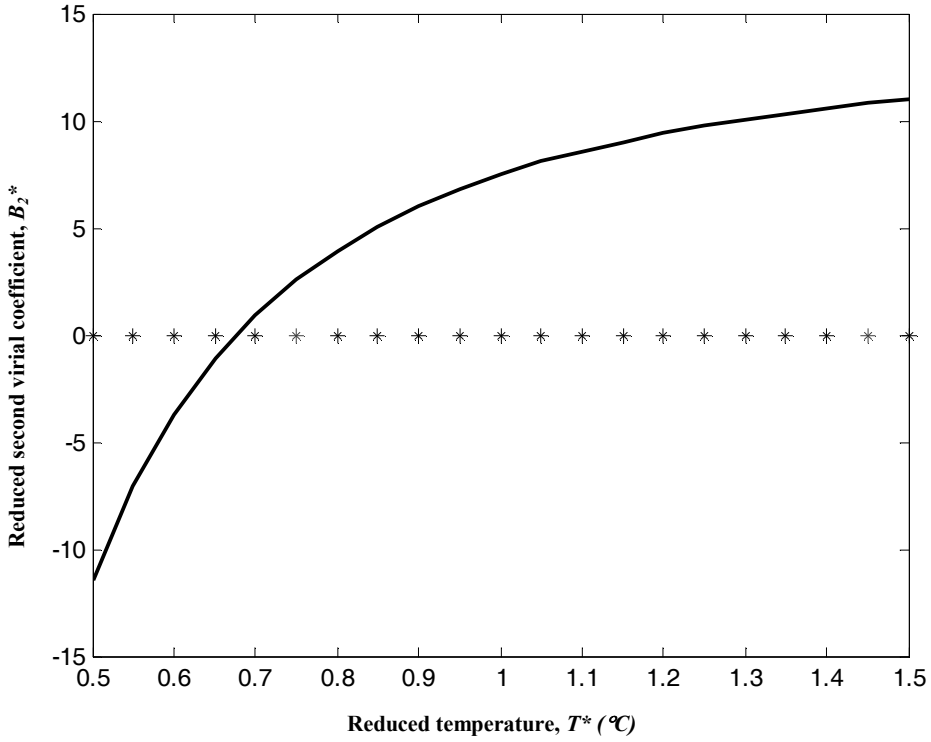

Figure 2. Reduced second virial coefficient (B_2*) versus reduced temperature (T*), solid line is this work and (*) is original LJD.

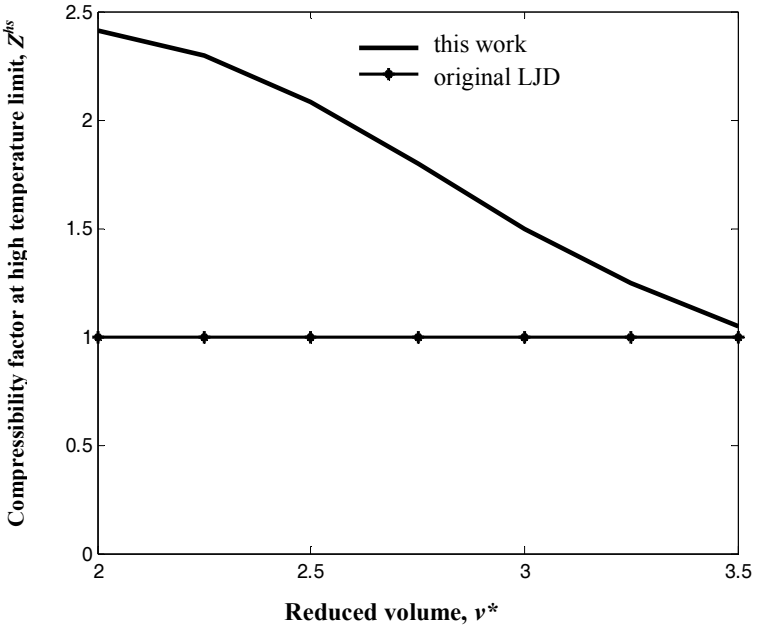

Figure 3. Compressibility factor at high temperature limit (Z^{hs}) versus reduced volume v*

Nomenclature

a	The distance between two neighboring molecules
a_0, a_1, a_2	Constants of proposed equation for coordination number
B_2	Second virial coefficient
B_2^*	Reduced second virial coefficient
C	Coordination number (a constant in LJD Theory)
g, g_l, g_m	Functions of y
G, G_l, G_m	Functions of y
h	Plank's constant
k	Boltzmann constant
l(y), m(y)	Functions of y, defined by equations 8 and 9, respectively when interactions with only the first shell of nearest neighbors are considered.
L(y), M(y)	Functions of y, defined by equations 12 and 13, respectively when interactions with the first three shells of nearest neighbors are considered.
m	Mass of a molecule
N	Number of molecules
P	Pressure
Q	Partition function
r	The distance of the wandering molecule from its lattice site
T	Temperature
T^*	Reduced Temperature
U	Internal energy
V	Total volume
v	Specific volume (V/N)
v_{cp}	Closed pack volume
v^*	Reduced volume (v/σ^3)
y	Dimensionless distance (r^2/a^2)
Z	Compressibility factor

Greek Letters

ε	Energy parameter in pair potential function
σ	Energy parameter in pair potential function
$\varphi(r)$	Total intermolecular force when the wanderer is at distance r from its lattice point

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