

Investigation of the Role of Coordination Number in the Lennard-Jones-Devonshire Theory*

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The theory of Lennard-Jones-Devonshire (LJD) has been studied for more than six decades by many researchers. Recently, Magee and Wilding have shown that in addition to the critical point originally reported for the 12–6 Lennard-Jones potential, the model exhibits a further critical point. In the present work, the effect of coordination number on the pressure-volume-temperature behavior of systems represented by the LJD-based equation of state was investigated. It was found that by varying the value of coordination number (C), different curves of P^* (dimensionless pressure) versus v^* (dimensionless volume) can be obtained for a specific T^* (reduced temperature). Consequently, improved representations of experimental data can be obtained by taking advantage of this characteristic of the $P^*-v^*-T^*-C$ relationship.

INTRODUCTION

Based on detailed statistical mechanical arguments, the final result of the LJD theory in the form of an equation of state can be represented by the following equations:^{1,2}

$$\frac{PV}{NkT} = 1 + \frac{24}{T^*} \left[\frac{1}{v^{*4}} \left(1 + \frac{2g_l}{g} \right) - \frac{1}{v^{*2}} \left(1 + \frac{2g_m}{g} \right) \right] \quad (1)$$

where T^* is reduced temperature and v^* is reduced volume according to the following definitions,

$$T^* = \frac{kT}{\varepsilon} \quad (2)$$

and

$$v^* = \frac{v}{\sigma^3} \quad (3)$$

ε and σ are the parameters of the Lennard-Jones potential function (potential 6–12):

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (4)$$

and,

$$g = \int_0^{y_0} \sqrt{y} \exp \left\{ -\frac{12}{T^*} \left[\frac{l(y)}{v^{*4}} - 2 \frac{m(y)}{v^{*2}} \right] \right\} dy \quad (5)$$

$$g_l = \int_0^{y_0} l(y) \sqrt{y} \exp \left\{ -\frac{12}{T^*} \left[\frac{l(y)}{v^{*4}} - 2 \frac{m(y)}{v^{*2}} \right] \right\} dy \quad (6)$$

$$g_m = \int_0^{y_0} m(y) \sqrt{y} \exp \left\{ -\frac{12}{T^*} \left[\frac{l(y)}{v^{*4}} - 2 \frac{m(y)}{v^{*2}} \right] \right\} dy \quad (7)$$

$$y_0 = (3/4\pi\sqrt{2})^{2/3} \quad (8)$$

* Dedicated to Professor Haruo Hosoya in happy celebration of his 70th birthday.

$$l(y) = (1+12y+25.2y^2+12y^3+y^4)(1-y)^{-10} - 1 \quad (9)$$

$$m(y) = (1+y)(1-y)^{-4} - 1 \quad (10)$$

In the original theory, the coordination number (C) was assumed constant and equal to 12.

As it can be seen from the above equations, the LJD theory is formulated in terms of only two molecular parameters that govern the intermolecular potential.¹ These parameters can, in principle, be calculated from quantum mechanics, and so the LJD theory is, in a sense, a completely molecular theory.² This is the main characteristic of the LJD theory, which distinguishes it from other similar theories such as significant structures. This fact is the main reason for continuing research work on this theory regardless of more than six decades of its original appearance.³ Nevertheless, it must be mentioned that poorer overall agreement with experimental data has been the price it has paid regarding the fundamental basis of the theory. Recently, several attempts have been made of improving the Lennard-Jones-Devonshire theory to predict liquid-solid and liquid-vapor phase transitions.^{4,5} In these work, the original potential energy model was changed for better agreement between theory and experimental data. In these improvements, the well-known original potential function (Lennard-Jones 12-6 potential function) has been altered. Here, for the sake of minimizing changes to the original theory, an attempt has been made to improve the theory and achieve better agreement with experimental data without changing the its overall molecular aspect. This work was carried out by considering the coordination number as a variable instead of a constant.

THE REVISED LJD THEORY

In the first step of this work it has been demonstrated that by choosing various coordination number values, different P - V diagrams may be obtained. It means that coordination number, which in the original theory was taken as a

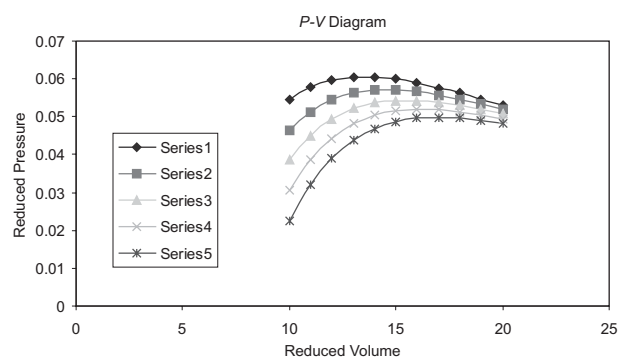


Figure 1. Various P^* - v^* isotherms for different coordination numbers (C). Symbols: * for $C = 10$; \times for $C = 11$; \blacktriangle for $C = 12$; \blacksquare for $C = 13$, and \blacklozenge for $C = 14$.

TABLE I. Comparison of the calculation results of the revised LJD theory with the original theory as well as experimental data for argon

v^*	$T^* = 2.808$			$T^* = 3.413$		
	Z(orig.)	Z(exp.)	Z(new)	Z(orig.)	Z(exp.)	Z(new)
2.944	1.64	1.14	1.12	1.76	1.25	1.23
2.219	1.87	1.36	1.43	2.02	1.50	1.57
1.851	2.09	1.64	1.79	2.28	1.80	1.88
1.488	2.51	2.34	2.31	2.74	2.32	2.28

constant ($C = 12$), could be used as a fitting parameter to achieve better agreement with experimental PVT data. To justify this idea, calculations have been carried out to produce different P - V diagrams resulting from various coordination number values. This point is demonstrated in Figure 1. In this figure, P^* - v^* (reduced pressure versus reduced volume) diagrams are presented for various coordination numbers without considering any particular fluid. In the following step, various calculations were made on different fluids, including hydrogen, nitrogen and argon. In these calculations, the proper value of the coordination number was found to achieve the best agreement with the experimental data. Optimization of the coordination number parameter could be carried out by comparison of the experimental data with the results of calculations. For this purpose, the following equation should be solved:

$$Z_{\text{exp}} = 1 + f(C, v_{\text{exp}}^*, T_{\text{exp}}^*) \quad (11)$$

where f is a complicated function based on the LJD theory. It must be emphasized again that at this stage C must be included as a parameter (not constant like in the original theory, which was 12). Here is the system of equations that must be applied in calculations:

$$f = \frac{2C}{T^*} \left[\frac{1}{v^{*4}} \left(1 + \frac{2g_l}{g} \right) - \frac{1}{v^{*2}} \left(1 + \frac{2g_m}{g} \right) \right] \quad (12)$$

$$g = \int_0^{y_0} \sqrt{y} \exp \left\{ -\frac{C}{T^*} \left[\frac{l(y)}{v^{*4}} - 2 \frac{m(y)}{v^{*2}} \right] \right\} dy \quad (13)$$

$$g_l = \int_0^{y_0} l(y) \sqrt{y} \exp \left\{ -\frac{C}{T^*} \left[\frac{l(y)}{v^{*4}} - 2 \frac{m(y)}{v^{*2}} \right] \right\} dy \quad (14)$$

$$g_m = \int_0^{y_0} m(y) \sqrt{y} \exp \left\{ -\frac{C}{T^*} \left[\frac{l(y)}{v^{*4}} - 2 \frac{m(y)}{v^{*2}} \right] \right\} dy \quad (15)$$

The results of our calculations are shown in Tables I–III.

TABLE II. Comparison of the calculation results of the revised LJD theory with the original theory as well as experimental data for nitrogen

v^*	$T^* = 2.987$			$T^* = 3.533$			$T^* = 4.080$		
	Z(orig.)	Z(exp.)	Z(new)	Z(orig.)	Z(exp.)	Z(new)	Z(orig.)	Z(exp.)	Z(new)
3.998	1.41	1.03	1.01	1.44	1.11	1.07	1.46	1.16	1.11
3.337	1.62	1.07	1.07	1.70	1.16	1.20	1.75	1.22	1.29
2.368	1.87	1.25	1.55	1.98	1.37	1.80	2.06	1.46	1.93
1.794	2.21	1.63	2.28	2.36	1.79	2.40	2.46	1.89	2.46
1.290	3.07	3.03	2.94	3.28	3.17	3.01	3.40	3.25	3.05

TABLE III. Comparison of the calculation results of the revised LJD theory with the original theory as well as experimental data for hydrogen

v^*	$T^* = 8.20$			$T^* = 9.70$			$T^* = 12.71$		
	Z(orig.)	Z(exp.)	Z(new)	Z(orig.)	Z(exp.)	Z(new)	Z(orig.)	Z(exp.)	Z(new)
1.878	2.61	2.12	2.08	2.63	2.10	2.04	2.62	2.05	2.02
2.108	2.42	1.91	2.05	2.43	1.90	2.01	2.43	1.87	1.99
2.442	2.22	1.71	1.97	2.23	1.70	1.96	2.22	1.69	1.95
2.946	1.98	1.52	1.73	1.98	1.53	1.74	1.93	1.52	1.73
3.640	1.59	1.38	1.42	1.54	1.39	1.42	1.50	1.39	1.43
4.082	1.34	1.32	1.26	1.31	1.33	1.26	1.28	1.33	1.27

 TABLE IV. Relations of a and b in Eq. (16) for different fluids

Fluid	$a(v^*)$	$b(v^*)$
Argon	$0.915 - 0.58v^*$	$-0.265 + 0.204v^*$
Nitrogen	$0.549 - 0.82v^*$	$0.020 + 0.231v^*$
Hydrogen	$2.559 - 0.93v^*$	$-0.850 + 0.45v^*$

Using the best values of C calculated for the best fits, we can see that at constant reduced volume there is a linear relationship between C and reduced temperature. Therefore, the following equation can be presented:

$$C = a(v^*) + b(v^*)T^* \quad (16)$$

where the relations for a and b are given in Table IV.

AGREEMENT OF OTHER EQUATIONS OF STATE WITH THE LJD THEORY

Since the LJD theory has a sound theoretical basis from the molecular point of view, it is important to compare it with the other important class of equations of state, namely cubic equations of state. As we know, these equations of state have an important role in industrial applications but most of them have no sound theoretical bases. At this stage, we want to compare some of the best known equations of state with the LJD theory as a completely molecular theory. These equations of state are the van der Waals (VDW), Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK), and Peng-Robinson (PR)

equations in the historical order of their appearance. For this examination, we can write the LJD equation of state in the following form:

$$Z = Z(T, v, \sigma, \varepsilon, C) \quad (17)$$

Hence, we can say that the compressibility factor is a function of two variables, T and v , as well as three parameters that reflect the nature of a fluid. These parameters are the Lennard-Jones potential function parameters and coordination number. This is quite consistent with the corresponding three parameter state theorem, in which there are two critical constants as well as a third parameter. This parameter is an acentric factor that is characteristic of a specific fluid.

After converting the above mentioned equations of state to the explicit form of compressibility factor, we can see that only two equations are consistent with the LJD theory. These equations of state are SRK and PR and can be written in the following form:

$$Z = Z(T, v, T_C, P_C, \omega) \quad (18)$$

Comparison between Eqs. (17) and (18) shows that SRK and PR equations of state are in good agreement with the molecular theory of LJD.

CONCLUSIONS

In this work, by developing a revised LJD theory, better agreement has been obtained between the experimental

data and the calculated results. It has been demonstrated that coordination number could be an important parameter for excellent fitting of experimental data and calculation results. Although the overall agreement is better in the case of the revised LJD theory, some facts can be mentioned here. Data in Table II show that in the case of nitrogen, the revised LJD theory has better agreement with experiment with respect to high reduced volume v^* , while for low reduced volume the old LJD theory has better agreement with experiment. To explain this fact, it may be mentioned that in low reduced volumes there is a more compact system of molecules, which exhibit a solid like lattice with a high coordination number (around 12, which is the coordination number in the original LJD theory). Moreover, as it can be seen in Table III, there is opposite behavior in the case of hydrogen. More powerful molecular thermodynamic models are needed to explain this behavior, but it can be said that hydrogen is a complex fluid that exhibits the hydrogen bonding phenomenon which affects its behavior. It has been shown

that the revised LJD theory, as a completely molecular theory, can produce excellent results in comparison with the experimental data. Moreover, a few well-known cubic equations of state, such as SRK and PR, could be recast in this new theory to find a sound theoretical basis.

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SAŽETAK

Istraživanje uloge koordinacijskog broja u Lennard-Jones-Devonshireovoj teoriji

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Kroz više od šest desetljeća mnogi su istraživači proučavali Lennard-Jones-Devonshireovu (LJD) teoriju. Nedavno su Maggie i Wilding pokazali da kritična točka u izvornoj LJD teoriji za 12–6 potencijal predviđa koegzistenciju kruto-tekuće, a ne prijelaz tekućina-plin kako je izvorno postulirano. U ovom se radu ispituje utjecaj koordinacijskog broja na ponašanje tlak-volumen-temperatura za sustave opisane LJD jednadžbom stanja. Pokazano je da se za zadanu T^* (reducirana temperatura) mijenjanjem koordinacijskog broja (C) dobivaju različite krivulje ovisnosti P^* (bezdimenzijski tlak) o v^* (bezdimenzijski volumen). Korištenjem ovako dobivenih $P^*-v^*-T^*-C$ dijagrama mogu se bolje prikazati eksperimentalni podaci.