

## Flexible equation of state for a hard sphere and Lennard–Jones fluid near critical temperature

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**Abstract.** Author uses the condition in terms of contact point radial distribution function  $G(\sigma, \lambda(\eta_c, \alpha))$  containing the self-consistent function  $\lambda(\eta_c, \alpha)$  and condition of continuity at  $\sigma/2 =$  contact point, to determine equation of state, (EoS). Different EoSs in terms of built-in parameter,  $m$ , can be obtained with a suitable choice of  $\lambda(\eta_c, \alpha)$  and the present EoSs have less r.m.s. deviation than Barker–Henderson BH2 for LJ fluids, and results are much closer to molecular dynamics (MD) simulations than expectations and reproduce the existing simulation data and present EoS for LJ potential, with the help of a set of minimum single-scaled parameter,  $a_0(\eta_c, \alpha)$  for a given reduced temperature,  $T^* = (1/\beta\epsilon) = 1.4, 2, 3, 4, 5, 6$ . It has been found that parameter  $\alpha = 1.059128388$  can be used to fix up the critical temperature parameter  $T_c = 1.3120(7)$  to that of a computer simulation result.

**Keywords.** Equation of state; Lennard–Jones potential; hard-sphere potential; liquid mixture; computer simulation.

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### 1. Introduction

There has been considerable progress during the past few years in developing equations of state, EoS, based on fundamental theories of statistical thermodynamics [1–4]. Naturally, a large number of adjustable parameters gives the equation sufficient flexibility to correlate data accurately over a wide range of state conditions. Many EoSs have been proposed based [5–12] on scaled particle theory (SPT). In a very broad way, a perturbing parameter can be introduced in a potential function. Let  $\lambda = \lambda_0$  represents a simple system with known properties and  $\lambda = \lambda_1$  can be a system under consideration. This leads to perturbation theories, which require only information of reference system. Many workers, such as Robles and de Haro [13] used Carnahan–Starling (CS) as a reference system. Wu and Sadus [14] conducted comparative studies of EoS for HS. Khasare [15] used strong repulsive potential together with a weak short-range attractive potential. Hard

sphere liquids can be considered as ideal liquids and are simple three-dimensional systems for study.

### 1.1 Motivation for the present work

The disadvantage of old modified equation of state is that it contains more than two model parameters, that is EoS became empirical in nature and many times it is not reliable outside the range for which the parameters were determined and may even give unphysical results. In this background, the present paper is an important [16–20] extension by inducting one more additional physical parameter and not the mathematical parameter, to fit available computer simulation data (Barker and Henderson, *Rev. Mod. Phys.* **48**(4), 587 (1976)) result [21] for the LJ fluid to an analytical EoS. It is observed that equation [22] can be used for estimating [23] nanosized spherical cavity in liquid and also for studying nanocavity-dependent [24] thermodynamics of Lennard–Jones biofluid.

## 2. Theory

Author has earlier [16–20] followed the result in terms of standard notations such as  $P$  is the pressure,  $\rho$  is the number density,  $T$  is the temperature and  $K_B$  is the Boltzmann constant.

$$\frac{\beta P}{\rho} = z_0 + z_1, \quad \beta = \frac{1}{K_B T}, \quad (1)$$

where

$$z_0 = \frac{(F_0 + F_1\eta + F_2\eta^2)}{(G_0 + G_1\eta)(1 - \eta)^2},$$

$$F_0 = -\lambda^{(m+1)}m; \quad F_1 = 4 + 2\lambda^{(m+1)}m - 4m\lambda^m - 4\lambda^m;$$

$$F_2 = -\lambda^{(m+1)}m + 4m\lambda^m - 8\lambda^m + 8;$$

$$G_0 = -\lambda^{(m+1)}m; \quad G_1 = -4\lambda^m - 4m\lambda^m + 4\lambda^{(m+1)}m + 4. \quad (2)$$

$$z_1 = \frac{(F_0 + F_1\eta)}{(G_0 + G_1\eta)}, \quad (3)$$

where

$$F_0 = 0;$$

$$F_1 = 4\beta\epsilon(\lambda^m f_1 + \lambda^m f_1 m - f_1 + \lambda^m f_2\beta\epsilon + \lambda^m f_2\beta\epsilon m - f_2\beta\epsilon);$$

$$G_0 = -\lambda^{(m+1)}m;$$

$$G_1 = -4\lambda^m - 4m\lambda^m + 4\lambda^{(m+1)}m + 4.$$

And for pure liquid, we have [18–20] the following:

$$(\lambda - 1) = \exp[k_c(\eta_c, \alpha)(f_1(\alpha)\beta\epsilon + f_2(\alpha)\beta^2\epsilon^2)\eta],$$

$$(\lambda - 1) = \exp\left[k_c(\eta_c, \alpha)\eta\left(\frac{8}{3}\beta\epsilon + \frac{64}{105}\beta^2\epsilon^2\right)\right], \quad \alpha = 1.$$

$$f_1(\alpha) = -\frac{4}{3}\alpha^6(\alpha^6 - 3), \quad f_2(\alpha) = \frac{8}{105}\alpha^{12}(15\alpha^{12} - 42\alpha^6 + 35), \quad (4)$$

where  $\lambda$  is a suitable density- and temperature-dependent function.  $k_c(\eta_c, \alpha)$  is a suitable constant and it is arbitrarily found out.

**Case** ( $m = m_1 = 0.5, \alpha^6 = 1$ ).

In order to get root mean square deviation (RMSD) to be minimum selecting  $k_c(\eta_c, \alpha) = k_{c1} = 0.1142022080$ , we obtained  $k_c(\eta_c, \alpha)$  by numerical technique yielding the following critical constant:

$$(\eta)_c = 0.1585689590, \quad (\beta\epsilon)_c = 0.8760646994.$$

For  $k_{c1}$ , the results computed are now better than the results computed by Barker and Henderson’s (BH) second-order perturbation approach.

For  $m = 0.50, \alpha = 1$  and in terms of significant figures,  $k_c = k_{c1} = 0.1142$ , we have the following results for equation of state:

$$\frac{\beta P}{\rho} = Z1(\text{SBK}). \tag{5}$$

It is observed that r.m.s. deviation  $Z(\text{SBK}) = 0.0387$ , while r.m.s. deviation  $Z(\text{BH2}) = 0.0416$  (see table 2).

### 3. Results

If the result is represented in graphical form, then, we get overlap curve for the present calculation with the computer simulation result. Hence, here, the results are presented in tabular form. The required hard-sphere contribution to LJ fluid is shown in table 1. We have carried out the comparative study of compressibility factor  $Z$  for different EoSs for Lennard–Jones liquid (table 2), where  $Z1 = Z1(\text{SBK}), m = 1/2, Z2 = Z2(\text{SBK}), m = 1/3, Z3 = Z(\text{CS})$  denote different EoSs in table 1, and  $Z1 = Z1(\text{SBK}), Z2 = Z(\text{BH2})$ , denote different EoSs in table 2.

**Table 1.** Ideal hard-sphere contribution for LJ potential ( $m = 1/2, k_c = 0$ ).

$\eta$	Z0(MD)	Z1(SBK)	Z2(SBK)	Z3(CS)
0.052	1.24	1.24	1.24	1.24
0.105	1.55	1.55	1.55	1.55
0.157	1.96	1.97	1.97	1.97
0.209	2.52	2.53	2.52	2.52
0.262	3.27	3.28	3.27	3.26
0.314	4.29	4.31	4.29	4.28
0.367	5.71	5.76	5.71	5.71
0.419	7.73	7.83	7.73	7.75
0.471	10.70	10.86	10.67	10.75
0.524	15.00	15.42	15.05	15.30

**Table 2.** Self-consistent EoS for LJ fluid at critical temperature ( $m = 0.50$ ,  $k_c = k_{c1}$ ).

$\eta$	Z0(MD)	Z1(SBK)	Z2(BH2)
0.052	0.72	0.76	0.74
0.105	0.50	0.54	0.52
0.157	0.35	0.38	0.36
0.209	0.27	0.30	0.26
0.262	0.30	0.35	0.27
0.288	0.41	0.45	0.35
0.340	0.80	0.87	0.74
0.393	1.73	1.74	1.64
0.445	3.37	3.36	3.36
0.497	6.32	6.32	6.32

**Table 3.** Parameters for LJ fluid at reduced temperature  $T^* = 1.4$  ( $m = 1/3$ ).

$T_c(\alpha)$	$a_1(\eta_c)$	$a_2(\alpha)$	$(\eta)_c$	$(\beta\epsilon)_c$	$\alpha^6$	rmsdev( $a_0$ )
1.18405	0.02380	0.974	0.1575021014	0.8445592094	1.067460	0.06256462002
1.31207	0.02380	0.974	0.1575021014	0.8234757552	1.411535	0.06243721727
1.31207	-0.4962	0.974	0.1654572122	0.7542008435	1.411535	1.35925474800

**Table 4.** Parameters for LJ fluid at different reduced temperatures ( $m = 1/3$ ,  $\alpha^6 = 1$ ).

$T^*$	$a_1(\eta_c)$	$a_2(\alpha)$	$(\eta)_c$	$(\beta\epsilon)_c$	$a_0(\eta_c, \alpha)$	rmsdev( $a_0$ )
1.4	0.0238	0.974	0.1575021014	0.8676235018	0.06399320052	0.06253392123
2.0	-0.201	0.766	0.1602420018	0.8234757552	-0.3868461586	0.03735314139
3.0	-0.790	0.570	0.1720803910	0.7542008435	-0.9946344339	0.04884071902
4.0	-1.471	0.474	0.1891343387	0.7096656437	-1.420966187	0.04854403523
5.0	-1.647	0.472	0.1930504869	0.7016268640	-1.564587647	0.04710652450
6.0	-2.911	0.373	0.2080304723	0.6703716541	-2.051982524	0.05283410682

**Table 5.** Parameters for LJ fluid at different reduced temperatures ( $m = 1/3$ ,  $\alpha^6 = 3$ ).

$T^*$	$a_1(\eta_c)$	$a_2(\alpha)$	$(\eta)_c$	$(\beta\epsilon)_c$	$a_0(\eta_c, \alpha)$	rmsdev( $a_0$ )
1.4	0.0238	0.984	0.1575021014	0.3031359118	0.06389072353	0.06234481541
2.0	-0.201	0.859	0.1602420018	0.2940768383	-0.3869901401	0.03741345520
3.0	-0.790	0.732	0.1720803910	0.2795540317	-0.9981059562	0.04730633480
4.0	-1.471	0.664	0.1891343387	0.2699948565	-1.426447154	0.04695860313
5.0	-1.647	0.658	0.1930504869	0.2682490094	-1.548165959	0.04234728193
6.0	-2.911	0.58497	0.2080304723	0.2613977248	-2.053566985	0.05283426583

**Table 6.** EoS for LJ fluid at reduced temperature ( $m = 1/3$ ).

$\eta$	Z0(MD)(1.4)	Z1(SBK)(1.4)	Z0(MD)(2.0)	Z1(SBK)(2.0)
0.052	0.74	0.77	0.89	0.89
0.105	0.54	0.57	0.82	0.82
0.157	0.41	0.43	0.82	0.81
0.209	0.35	0.37	0.88	0.89
0.262	0.40	0.44	1.07	1.10
0.314	0.67	0.73	1.46	1.50
0.367	1.32	1.34	2.16	2.18
0.419	2.55	2.48	3.30	3.27
0.471	4.60	4.46	5.07	4.98
0.524	7.76	7.83	7.60	7.65

**Table 7.** EoS for LJ fluid at reduced temperature ( $m = 1/3$ ).

$\eta$	Z0(MD)(3.0)	Z1(SBK)(3.0)	Z0(MD)(4.0)	Z1(SBK)(4.0)
0.052	0.99	1.00	1.04	1.05
0.105	1.02	1.04	1.12	1.14
0.157	1.11	1.14	1.25	1.29
0.209	1.27	1.33	1.45	1.52
0.262	1.56	1.63	1.77	1.84
0.314	2.00	2.09	2.22	2.22
0.367	2.69	2.76	2.87	2.93
0.419	3.72	3.72	3.79	3.81
0.471	5.17	5.12	5.07	5.04
0.524	7.17	7.16	6.78	6.76

**Table 8.** EoS for LJ fluid at reduced temperature ( $m = 1/3$ ).

$\eta$	Z0(MD)(5.0)	Z1(SBK)(5.0)	Z0(MD)(6.0)	Z1(SBK)(6.0)
0.052	1.06	1.05	1.08	1.09
0.105	1.12	1.14	1.20	1.23
0.157	1.32	1.29	1.37	1.41
0.209	1.54	1.51	1.60	1.66
0.262	1.87	1.83	1.92	2.00
0.314	2.32	2.27	2.36	2.44
0.367	2.94	2.88	2.96	3.01
0.419	3.78	3.72	3.85	3.77
0.471	4.94	4.87	4.82	4.79
0.524	6.45	6.49	6.18	6.17

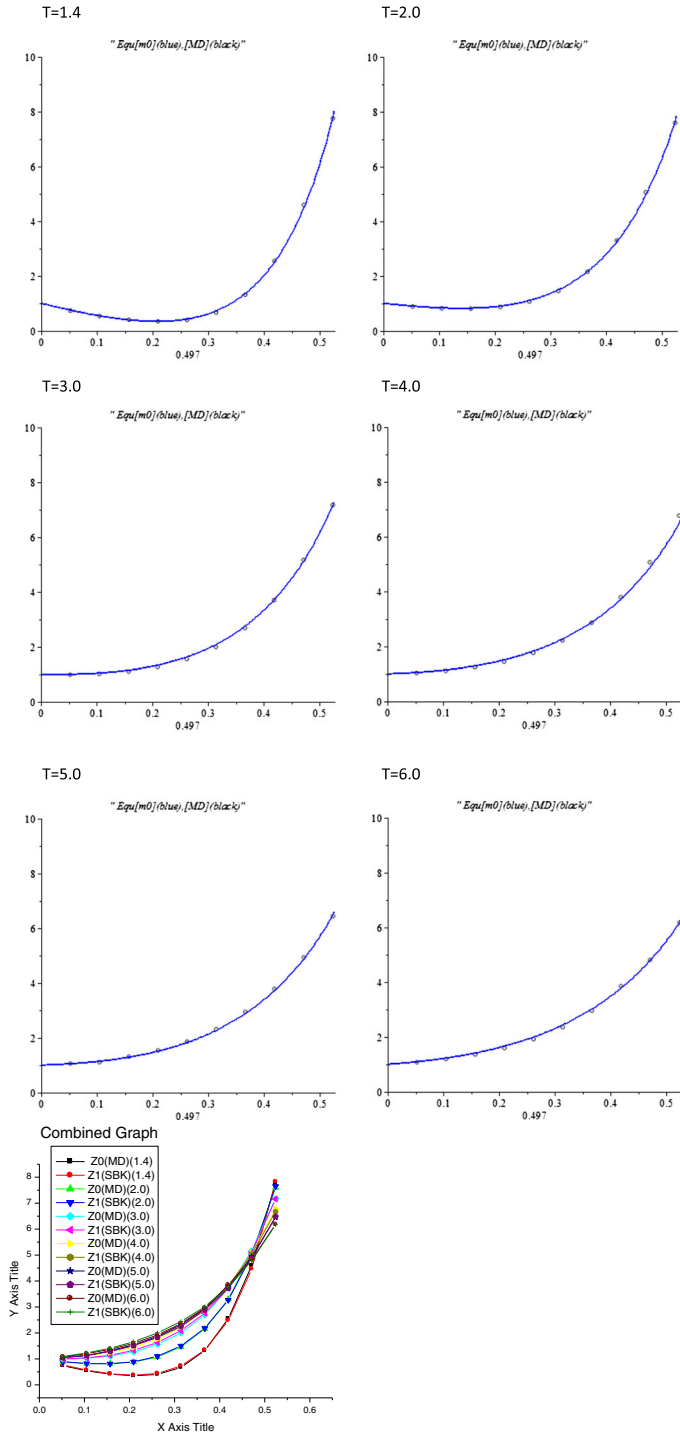


Figure 1. Graphical representations corresponding to tables 6–8.

It is observed from tables 3, 4 and 5 that, by introducing two arbitrary scaling parameters  $a_1(\eta_c)$  and  $a_2(\alpha)$  corresponding to each reduced temperature,  $T^*$ , we can reproduce (see tables 6, 7 and 8)  $Z(\text{MD})$  results by the present flexible  $Z1(\text{SBK})$  equation.

It is observed that eq. (6) is stronger in simulation data reproducing

$$\begin{aligned}\lambda &= 1 + \exp[a_0(\alpha)\eta^{1/3}], \\ a_0(\alpha) &= [f_1(\alpha)\beta\epsilon + f_2(\alpha)(\beta\epsilon)^2], \quad \epsilon = a_1(\alpha)\epsilon_c.\end{aligned}\quad (6)$$

#### 4. Conclusion

If we select  $k_c(\eta_c, \alpha) = k_c$  by the numerical technique, for tables 1 and 2 then, one may say that the present formulation is good.

It can be seen from table 3 that for getting good estimate of critical constant ( $T_c, \eta_c$ ) one has to forget  $\text{rmsdev}(a_0)$  as it is 1.3592, indicating bad values of  $Z(m)$ . However, one can achieve good estimate of critical temperature only, by selecting  $\alpha$ , keeping  $\text{rmsdev}(a_0) = 0.06243$ , indicating remarkable values of  $Z(m)$  over the entire range of reduced density ( $0 < \rho d^3 < 1.0$ ), i.e.  $0 < \eta < \pi/6$ , but this is not possible for ( $\eta_c$ ) through any value of  $\alpha$ , i.e. it always gives very poor  $\text{rmsdev}(a_0)$ . In the above conclusion, we find  $\text{rmsdev}(a_0)$  by using  $T^* = 1.4$ .

From tables 4 and 5, it is observed that by selecting  $a_0$ ,  $Z0(\text{MD})$  results can be reproduced, i.e.  $\text{rmsdev}$  should be minimum. Similarly,  $a_1(\eta_c)$  and  $a_2(\eta_c)$  seem to be functionally connected with  $a_0$  and choice of  $\alpha$  decides the magnitude of  $(\beta\epsilon)_c$ .

Functional investigation in terms of  $\lambda$  open up density- and temperature-dependent views at the contact point of molecules in fluid state, though they are interacting through the same pair potential. This equation accurately correlates  $Z$  from the triple point to about 4.5 times the critical temperature  $T^*$  over the entire fluid range with the help of two line parameters  $a_1(\eta_c)$  first-physical and  $a_2(\alpha)$  second-physical or equivalently single parameter on scaled-surface  $a_0(\eta_c, \alpha)$  (see tables 6, 7 and 8 and figure 1). It is easy to understand up to two parameters because interaction potential contains a minimum of two physical parameters.

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