

EQUATION OF STATE OF A LENNARD-JONES 12-6 PAIRWISE ADDITIVE FLUID

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Dedicated to Professor Dr E. Hála on the occasion of his 60th birthday.

An empirical equation of state was proposed, which is based on pseudoexperimental data on the state behaviour. The equation can be used at reduced temperatures from the range 0.7–100.0 and reduced densities up to 2. Calculated compressibility factors and critical properties agree well with available literature data.

Models of fluid state are often tested on so-called pseudoexperimental data on the state behaviour, which are obtained by computer simulation using the Monte-Carlo¹⁻³ and molecular dynamics^{4,5} methods. A comparison with these data can be employed for separating inaccuracies of the model from our incomplete knowledge of intermolecular potentials.

So far, a relatively large amount of these data has been generated and published but they are scattered in papers by many authors^{2,5-18}. An analytical representation of machine data is more advantageous since it allows one to test the theories in a wide and continuous range of temperatures and densities more easily as well as it enables to calculate and compare thermodynamic quantities which cannot be determined directly from experiment.

McDonald and Singer published an equation of state¹³, which is an analytical representation of their pseudoexperimental data calculated with the Lennard-Jones potential. The range of validity of this equation is consequently limited only to the region of the reduced temperature $\tilde{T} \in \langle 0.55, 1.235 \rangle$ and reduced density $\tilde{\rho} \in \langle 0.63, 0.96 \rangle$ (see relation (1)) and constants in this equation were adjusted only to data of its authors.

Therefore, it is the aim of our work to propose an equation of state for a Lennard-Jones 12-6 fluid, which would fit the simulated data with "experimental" accuracy in both the gaseous and liquid phases.

The first part comprises the analysis of the pseudoexperimental data, the second part presents a new form of the equation of state, whereas calculated compressibility factors and critical properties are discussed in the third part.

Pseudoexperimental Data

A literature survey of published equilibrium data^{2,5-18} calculated by the Monte-Carlo and molecular dynamics methods gave approximately 400 compressibility factors at various reduced temperatures \tilde{T} and reduced densities $\tilde{\rho}$. The reduced variables are given by

$$\tilde{T} = kT/\varepsilon \quad \tilde{\rho} = N\sigma^3\rho \quad \tilde{p} = p\sigma^3/\varepsilon, \quad (1)$$

where k is Boltzmann's constants, ε , σ parameters of the Lennard-Jones potential, T absolute temperature, ρ density, p pressure. The machine data are in the ranges

$$\tilde{T} \in \langle 0.6, 100.0 \rangle$$

$$\tilde{\rho} \in \langle 0.02, 5.0 \rangle$$

$$z \in \langle -2.05, 348.0 \rangle,$$

where $z = \tilde{p}/\tilde{T}\tilde{\rho}$. The data are loaded with an error of the machine experiment. Statistically estimated error of these machine data is within the range of z between 0.01 and 0.1. Wood¹⁸ presents the following figures: the region of low compressibility factors-error 0.04-0.07; the region of the gaseous phase-error ~ 0.01 ; the region of the liquid phase-error 0.05-0.1.

Sometimes the authors are less modest in estimating errors of their own data and sometimes they do not report them at all. Due to these reasons and also owing to the fact that the authors do not present any data necessary for the choice of statistical weights of these data, we performed an analysis of the set of pseudoexperimental data (it is described in more detail in¹⁹). The pseudoexperimental points were ordered along isotherms and isochores. The best analytical expressions with respect to the minimal sum of squared deviations were found for each isotherm and isochore. For these analytical expressions, values of their adjustable constants were also calculated. This correlation gave a more objective basis for omission of "suspected" points (taking into account the graphical representation). Standard deviations of individual isotherms were used for estimating statistical weights of corresponding points. To avoid an undesirable preference of pseudoexperimental points in densely occupied regions, smoothed data, equidistant in density, were calculated from the correlation equations of corresponding isotherms. The smoothed data temperature range is $\tilde{T} \in \langle 0.7, 100.0 \rangle$ and the upper bound of density is found in Table I.

The following weights

$$w_i = 1/\sigma_i^2 \quad (2)$$

were assigned to the points, where σ_i is the standard deviation for the i th isotherm.

Equation of State

To express the smoothed data properly, more than 100 of different functional forms of the equation of state were tested and they were similar to those employed in the description of the state behaviour of cryogenic fluids. The following form proved most satisfactory

$$\begin{aligned}
 z(\tilde{v}, \tilde{T}) = & 1 + B_2(T) \tilde{v} + B_3(T) \tilde{v}^2 + d^3(C_1 + C_2/\tilde{T} + C_3/\tilde{T}^2 + C_4/\tilde{T}^3 + \\
 & + C_5/\tilde{T}^4) + d^4(C_6 + C_7/\tilde{T} + C_8/\tilde{T}^2 + C_9/\tilde{T}^3 + C_{10}/\tilde{T}^4) + \\
 & + d^5(C_{11} + C_{12}/\tilde{T}) + d^6[C_{13} \exp(-10d^2) + C_{14}/\tilde{T} + \\
 & + C_{15}/\tilde{T}^2 + C_{16}/\tilde{T}^3] + d^8[C_{17} \exp(-10d^2) + C_{18}/\tilde{T}] + \\
 & + d^{10}(C_{19} + C_{20}/\tilde{T}) + C_{21}d^{12}, \quad (3)
 \end{aligned}$$

where $d = \tilde{v}\tilde{T}^{-1/4}$, B_2 and B_3 are the second and third virial coefficients, resp., C_i 's are adjustable constants. Values of the constants as calculated by the weighted least squares method are:

$C_1 =$	6.936698	$C_{12} =$	-188.5400
$C_2 =$	-39.96676	$C_{13} =$	-113.3933
$C_3 =$	106.8000	$C_{13} =$	307.6045
$C_4 =$	-184.6228	$C_{15} =$	-67.09880
$C_5 =$	131.1701	$C_{16} =$	63.30742
$C_6 =$	26.39421	$C_{17} =$	37.71457
$C_7 =$	28.56095	$C_{18} =$	-226.6979
$C_8 =$	-28.04602	$C_{19} =$	55.9605
$C_9 =$	111.9788	$C_{20} =$	105.4608
$C_{10} =$	-123.5420	$C_{21} =$	-55.17528
$C_{11} =$	-20.61594		

TABLE I

Upper Limits to Density for Some Temperatures

\tilde{T}	0.7	0.9	1.15	1.35	2.74	5	20	100
\tilde{v}_{\max}	0.9	0.8	0.9	0.9	1.1	1.3	1.8	2.0

TABLE II
The Comparison of Calculated, z_{calc} , and Pseudoexperimental, z_{exp} , Compressibility Factors

\tilde{T}	\tilde{v}	z_{calc}	z_{exp}	Δz_{calc}	Ref.
0.72	0.8350	-0.54	-0.08	-0.46	13
0.72	0.8645	0.11	0.61	-0.50	13
0.72	0.8973	1.48	1.54	-0.06	13
0.81	0.7940	0.08	0.01	0.07	11
0.81	0.8480	1.02	1.01	0.01	12
0.81	0.8645	1.48	1.43	0.05	13
0.81	0.8830	2.12	2.06	0.06	12
1.06	0.6468	-0.01	-0.03	0.02	13
1.06	0.7311	0.57	0.59	-0.02	13
1.06	0.7847	1.24	1.23	0.01	13
1.06	0.8212	1.88	1.82	0.06	13
1.15	0.020	0.92	0.92	0.00	9
1.15	0.100	0.62	0.61	0.01	9
1.15	0.300	0.11	0.12	-0.01	9
1.15	0.600	0.06	0.07	-0.01	9
1.15	0.850	2.86	2.86	0.00	9
1.15	0.920	4.76	4.72	0.04	9
1.35	0.200	0.50	0.50	0.00	7
1.35	0.300	0.36	0.36	0.00	7
1.35	0.400	0.27	0.27	0.00	8
1.35	0.500	0.29	0.30	-0.01	8
1.35	0.550	0.38	0.41	-0.03	8
1.35	0.700	1.19	1.17	0.02	8
1.35	0.800	2.47	2.42	0.05	8
1.35	0.900	4.53	4.58	-0.05	8
2.74	0.550	1.65	1.65	0.00	8
2.74	0.700	2.55	2.59	-0.04	10
2.74	0.900	5.14	5.14	0.00	8
2.74	1.100	10.19	10.20	-0.01	10
5	0.500	1.85	1.87	-0.02	10
5	1.000	6.34	6.34	0.00	10
5	1.280	13.30	13.40	-0.10	10
20	0.500	1.95	1.89	0.06	10
20	1.000	4.45	4.46	-0.01	10
20	1.770	16.82	16.70	0.10	10

TABLE II
(continued)

\tilde{T}	$\tilde{\rho}$	z_{calc}	z_{exp}	Δz_{calc}	Ref.
100	0.500	1.68	1.67	0.01	10
100	1.000	2.96	2.95	0.01	10
100	1.400	4.72	4.76	-0.04	10
100	2.000	9.48	9.50	-0.02	10

The validity region of the equation of state is given by the region of the smoothed data and its upper bound in density can be found in Table I.

DISCUSSION

A comparison of compressibility factors calculated from the equation of state with the data is given in Table II.

It is obvious that somewhat higher deviations are encountered at temperatures near 0.7 and densities corresponding to the metastable region. Here, the lower accuracy can be brought about by the relatively low amount of reliable machine data.

At $\tilde{T} > 0.9$, the equation of state proposed gives good results and the deviations correspond to the pseudoexperimental error in order.

In the common region of validity we compared our results with the 16-constant equation by McDonald and Singer¹³

$$\begin{aligned}
 z = & (-2.5867799/\tilde{\rho} + 9.4946333 - 11.662612\tilde{\rho} + 4.7748408\tilde{\rho}^2)/\tilde{T} \\
 & + \ln(\tilde{T})(-5.1089184/\tilde{\rho} + 18.782851 - 23.086524\tilde{\rho} + \\
 & + 9.4576404\tilde{\rho}^2) + \tilde{T}(2.5434611/\tilde{\rho} - 9.2214710 + 11.163428\tilde{\rho} - \\
 & - 4.4867688\tilde{\rho}^2) + \tilde{T}^2(0.0328336/\tilde{\rho} - 0.2145368 + 0.3879144\tilde{\rho} \\
 & - 0.2181736\tilde{\rho}^2)
 \end{aligned} \quad (4)$$

whose region of validity is approximately $\tilde{T} \in \langle 0.55, 1.235 \rangle$ and $\tilde{\rho} \in \langle 0.63, 0.96 \rangle$. The comparison of values of z calculated from the equation proposed in our work with results of the McDonald and Singer equation was performed on machine data from which both authors had obtained constants in their correlation equation and it is given in Table III.

TABLE III

The Comparison of Deviations between Pseudoexperimental Data — z_{exp} — and Compressibility Factors Calculated from the Equation of State Proposed in this Paper — Δz_{calc} — or from the Equation¹³ — Δz_{DS}

\tilde{T}	\tilde{q}	z_{exp}	Δz_{calc}	Δz_{DS}
0.72	0.8350	-0.08	-0.46	-0.03
0.72	0.8839	1.11	-0.28	0.05
0.72	0.8973	1.54	-0.06	0.03
0.81	0.8010	0.06	0.10	0.00
0.81	0.8212	0.55	-0.09	-0.11
0.81	0.8839	2.06	0.10	0.10
0.902	0.7497	-0.13	0.24	0.08
0.902	0.7847	0.56	-0.06	-0.12
0.902	0.8484	1.56	0.13	0.11
0.902	0.8645	2.11	0.02	-0.05
0.977	0.7096	-0.04	0.12	0.02
0.977	0.7689	0.73	-0.08	-0.09
0.977	0.8350	1.81	-0.03	-0.02
1.06	0.6468	-0.03	0.01	-0.01
1.06	0.7497	0.78	-0.01	-0.01
1.06	0.7847	1.23	0.01	0.03
1.06	0.8212	1.82	0.07	0.07
1.135	0.6256	0.16	-0.05	0.01
1.135	0.7096	0.59	0.06	0.07
1.135	0.7689	1.15	0.17	0.19
1.135	0.7847	1.56	-0.01	0.01
1.235	0.6789	0.77	-0.06	-0.04
1.235	0.7311	1.18	0.00	0.02
1.235	0.7497	1.41	-0.01	0.01

As it could be expected, the McDonald and Singer equation fits substantially better the low-temperature data for the liquid phase. Although the equation proposed in our work was derived for a much wider range, its accuracy at $\tilde{T} > 0.9$ is comparable with their equation, which was obtained directly from this limited data set. However, it can be assumed that values of the thermodynamic functions calculated from the McDonald and Singer equation will be more accurate, since this equation was created by simultaneous correlation of the compressibility factor and internal energy.

The critical point is rather sensitive quantity and because of that it can be considered as a significant measure of quality of any equation of state. Verlet and Levesque⁸ present the following critical constants: $\hat{T}_c = 1.36 \pm 0.03$, $\hat{\rho}_c = 0.36 \pm 0.03$, $z_c = 0.31 \pm 0.03$; they were obtained by improving the PY 2 equation through the inclusion of pseudoexperimental data. The critical constants calculated from our equation of state proposed for a Lennard-Jones 12-6 fluid are

$$\hat{T}_c = 1.35 \quad \hat{\rho}_c = 0.33 \quad z_c = 0.33 .$$

We believe that the equation of state proposed can facilitate tests of the theories of simple fluids and that it can prove useful for perturbation methods based on the Lennard-Jones fluid and for determining thermodynamic functions which are not directly measurable.

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