Equation of state to predict the solid-liquid-vapor phase coexistences of pure substances

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A non-cubic equation of state is used to predict the solid-liquid, solid-vapor and liquid-vapor coexistences of pure substances. The equation of state is obtained using as input data the critical point, the boiling temperature, the triple point temperature and the acentric factor of the substance. In this work, some examples of phase diagrams predicted with the equation of state are reported in order to show its capabilities. Finally, a database with the parameters for different pure substances is presented.

Keywords: Phase coexistence; solid; liquid; vapor; pure substances.

1. Introduction

The liquid-vapor equilibrium of substances in engineering applications is modeled mainly with cubic equations of state (CEoS). This approximation is practical and useful when the substances are fluids, but cubic equations cannot predict the solid phase [1]. In this case, solid phase and its coexistence states can be addressed using a pseudo-mixture instead of the substance *per se*, *i.e.* the substance is considered as a "*mixture*" [2–4] with two or more components of the same substance. In this approximation, the main component is constituted by single molecules of the substance, while other components are constituted by molecular clusters (solid phase). Such pseudo-component differs from other only by the size of molecular cluster. Thus, the liquid and the vapor phases are described by the CEoS of the substance, while the solid phase (constituted by different sets of molecular clusters) is described with its corresponding CEoS at the "*mixture*".

Another approximation is by using a modified CEoS. The new equation of state is necessarily a Non-Cubic Equation of State (Non-CEoS). There are few analytical Non-CEoS in the literature [4–8], and all of them were designed to do possible a second loop to capture the solid-liquid coexistence (similar to the loop for the liquid-vapor coexistence in a conventional CEoS). The first example of a Non-CEoS corresponds to Wenzel's equation [5], and its subsequent modification [9], that captures some solid-liquid coexistence states, but it was not designed to avoid a solid-liquid critical point. At least in the literature, there is not evidence about the occurrence of such solid-liquid critical point.

In the second example, Yokozeki's equation introduces a factor with an un-physical discontinuity in the repulsion term

(see ref [10]). This discontinuity was introduced to avoid a solid-liquid critical point in an effective way [6, 7], but is unnecessary and do not have a plausible physical interpretation [10]. The third and final example was reported by Guevara and Romero [8] and its structure will be given in equation (1a) in the following section. In this case, the most general CEoS is modified with an additional attractive term [11], and the procedure to define this term implies that solid-liquid critical point does not exist at all.

In this work, the equation developed by Guevara and Romero [8] was applied to several substances to obtain the parameters that define this equation for each substance, and some phase diagrams are calculated to compare the prediction of coexistence states with experimental data. The procedure to obtain an expression of the Non-CEoS for a particular substance is described in Sec. 2; while the database of substances and its associated parameters are reported in Sec. 3, along with some graphical examples of three of the substances reported. Conclusions are in Sec. 4.

2. Defining Non-CEoS

The Non-CEoS reported in [8] is showed in Eq. (1a):

$$P(v,T) = P_0(v,T) - \frac{fT}{(v-e)^\nu}; \qquad (1a)$$

$$P_0(v,T) = \frac{RT}{v-b} - \frac{a(T)}{(v-c)(v-d)}; \qquad (1b)$$

$$a(T) = RT\big(b - B(T)\big); \qquad (1c)$$

$$B(T) = b\big(1 - (\lambda^3 - 1)(e^{\varepsilon/RT} - 1)\big). \qquad (1d)$$

In this case, the pressure P of the fluid is a function of the molar volume v, and the temperature T, while R is the gas constant ($= 83.14472$ cm^3 bar/Kelvin mol). The Non-CEoS is composed by a cubic equation of state P_0 plus an attractive term that is related to very short-range interactions between molecules of the substance. Thus, the attractive term affects the behavior of cubic equation only at a neighborhood of the exclusion volume b. In other words, vapor phase predicted by cubic equation practically does not change, because the short attractive term is negligible. However, solid phase appears due to this attractive term and is additional to the liquid and vapor phases predicted by P_0.

Cubic equation of state P_0 (Eq. 1b) take account of the mean size of molecules through the parameter b. The effect of mean-range interactions between molecules is considered through the attractive term, and is implicitly included in the function $a(T)$ through the second virial coefficient $B(T)$. The relation between $a(T)$ and $B(T)$ comes from the virial expansion of the equation of state, as shown in Eqs. (1c) and (1d), and the expression of $B(t)$ is the exact result derived from square-well potential (see Eq. (4), in Sec. 3). Square-well potential $u(r)$ captures the main features of a mean-range attraction between molecules and describes the liquid-vapor coexistence.

Finally, in order to define the analytical expression of the Non-CEoS for a particular substance is necessary to obtain the set of parameters $\{b, c, d, e, f, \lambda, \varepsilon\}$. These parameters are determined using the following experimental data of the substance: critical pressure P_c, critical molar volume v_c, and critical temperature T_c, the acentric factor ω, temperature T_b at the boiling point, and temperature T_t at the triple point. The exponent ν is also a parameter that can be adjusted according to the substance to be studied. For this work, an exponent of $\nu = 12$ was found adequate to represent the complete phase transitions curves of the reported substances.

3. Procedure to construct the equation of state

The first step in order to define the Non-CEoS is finding the parameters (b, c, d) that appear in Eqs. (1a)-(1d), using the liquid-vapor critical point defined by the coordinates (P_c, v_c, T_c). The Non-CEoS needs to fulfills the following conditions:

$$P(v_c, T_c) = P_c; \tag{2a}$$

$$\left(\frac{\partial P}{\partial v}\right)_{P_c, v_c, T_c} = 0; \tag{2b}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{P_c, v_c, T_c} = 0. \tag{2c}$$

To solve the previous system of equations is possible in the special case of a null attractive term in Eq. (1a), *i.e.* $f = 0$, that reduces (1a) to a cubic equation of state. In this case, parameters b, c, and d are determined from Eqs. (2a)-(2c), and their expressions [8, 11] are:

$$\frac{b}{v_c} = \frac{Z_c - 1 + \alpha_c}{Z_c}; \tag{3a}$$

$$\frac{c}{v_c} = \frac{Z_c - \frac{1}{2}\alpha_c + \alpha_c\sqrt{\alpha_c - \frac{3}{4}}}{Z_c}; \tag{3b}$$

$$\frac{d}{v_c} = \frac{Z_c - \frac{1}{2}\alpha_c - \alpha_c\sqrt{\alpha_c - \frac{3}{4}}}{Z_c}, \tag{3c}$$

where $Z_c = P_c V_c / R T_c$ is the critical compressibility and the value of α_c is related to $a(T_c)$ through: $\alpha_c^3 = P_c\, a(T_c)/R^2\, T_c^2$.

Equations (3a)-(3c) are valid if $f = 0$ in Eq. (1a). In this case, the "*critical point*" of cubic equation is equal to the experimental critical point of the substance. However, if $f > 0$, then the "*critical point*" of the cubic equation is slightly displaced with respect to the critical point of the substance. Thus, Eqs. (3a)-(3c) must be considered just as initial values for parameters b, c, and d.

Determining the value of parameter b enable us to define the repulsive term presented in Eq. (1a). After that, the next step is to define $a(T)$ (Eq. 1c) to obtain the second term of $P(0)$. $a(T)$ is defined through $B(T)$, which is the second virial coefficient. Therefore, to find $B(T)$ is equivalent to find $a(T)$. In this work, the second virial coefficient is derived from the square-well potential, namely,

$$u(r) = \begin{cases} +\infty, & \text{if} \quad r \leq \sigma; \\ -\varepsilon, & \text{if} \quad \sigma < r \leq \lambda\sigma. \\ 0, & \text{if} \quad \lambda\sigma < r, \end{cases} \tag{4}$$

where σ is the hard sphere diameter, λ is related to the width of the attractive part, ε is the square-well depth, and r is the radial distance between the centers of two spheres.

The second virial coefficient for this pair potential $u(r)$ has a simple and exact expression, shown in Eq. (1d). On the other hand, $a(T)$ must be a function of class C^2 [12, 13]: its first (da/dT) and second derivatives (d^2a/dT^2) exist and are continuous; it must be positive $(a > 0)$, monotonically decreasing $(da/dT < 0)$, and convex $(d^2a/dT^2 > 0)$; its third derivative (d^3a/dT^3) is negative for any value of the temperature T.

Therefore, $a(T)$ in Eq. (1c) fulfills with all above features only if $(2/3)\pi N_A \sigma^3 = b$, where N_A is the Avogadro's number. In consequence, second virial coefficient is defined with λ, and ε, in such a way that equation of state is anchored to acentric factor and boiling point temperature. The values of these parameters are determined by solving:

$$\omega(\lambda, \varepsilon) = \omega^{(\exp)} \tag{5}$$

$$T_b(\lambda, \varepsilon) = T_b^{(\exp)}, \tag{6}$$

where ω and T_b are the acentric factor and the boiling point temperature predicted by the Non-CEoS, while $\omega^{(\exp)}$ and $T^{(\exp)}$ are constants and come from experimental data of the

substance. After this procedure is done, the mean range attractive term of the auxiliary cubic equation of state is defined.

3.1. Non-CEoS and the Corresponding States Principle

For a given substance, the equation of state is defined using the following data: critical point, triple point temperature, acentric factor, and boiling point temperature. In particular, the Reduced Equation of State (RES) is constructed by rescaling the thermodynamics variables with its critical value. With this purpose, let us define the reduced variables $v_r \equiv v/v_c$, $T_r \equiv T/T_c$, and $P_r \equiv P/P_c$, and therefore, the equation of state is rewritten as

$$P_r = \frac{T_r}{Z_c(v_r - B)}$$
$$- \frac{\alpha^3(T_r)}{Z_c^2(v_r - C)(v_r - D)} - \frac{FT_r}{(v_r - E)^{12}}, \quad (7)$$

where $B = b/v_c$, $C = c/v_c$, $D = d/v_c$, $E = e/v_r$, $F = fT_c/P_c v_c^{12}$ and $\alpha^3(T_r) \equiv a(T)P_c/R^2 T_c^2$. Moreover, the second virial coefficient of the square-well potential is substituted into the definition of the function $\alpha^3(T_r)$, and the result is

$$\alpha^3(T_r) = \alpha_c^3 T_r \left[\frac{(1 + f_c)^{1/T_r} - 1}{f_c} \right], \quad (8)$$

where $f_c \equiv e^{\varepsilon/k_B T_c} - 1$.

The most important consequence of the Eqs. (7) and (8) is that *the RES is independent of the parameter λ (Eq. 1d). In other words, the RES fulfills the corresponding-states principle.* However, the equation of state does not describe a fluid with a pure square-well potential. In fact, only the second virial coefficient corresponds to the square-well model. Moreover, the square-well potential does not fulfill the corresponding-states principle because any change of the parameter λ corresponds to a non-conformal change of the potential. The last statement has been demonstrated in the work of Fernando del Rio *et al.* [14]. In consequence, the equation of state does not describe a fluid with the square-well potential. On the other hand, the RES is independent of λ, but the parameter λ does not have an arbitrary value because is determined through the experimental data of the substance.

3.2. Short range attractive term

The improvement of Eq. (1a) is its capacity to predict the solid-liquid and solid-vapor phase coexistences. The solid phase is additional to the liquid and vapor phases predicted by P_0, and the solid-fluid coexistence is related to a second calculation loop that appears because of the last term. The first calculation loop comes from the cubic equation of state P_0, and is related to the liquid-vapor phase coexistence up to the liquid-vapor critical point of the substance.

In order to define the parameters e and f, it is convenient to discuss the possible existence of a critical point in the solid-liquid region, which has been mentioned by other authors [5, 9]. A crucial characteristic of the liquid phase is that always has a non ordered configuration, while the solid phase is an ordered crystal. Therefore, a solid-liquid critical point must not exist because both phases are always distinguishable. Thus, the second calculation loop must never end at a solid-liquid critical point for any value of the temperature, and at the limit of high temperature, the next restriction for the equation of state must be fulfilled:

$$\lim_{T \to \infty} \frac{1}{T} \left(\frac{\partial P}{\partial v} \right) = 0. \quad (9)$$

In this work, the existence of two values $v_{\min}$ and $v_{\max}$ (with $b < v_{\min} < v_{\max} < v_c$) for molar volume in Eq. (9) are postulated. Consequently, the existence of $v_{\min}$ and $v_{\max}$ ensures that solid-liquid critical point does not exist for any value of the temperature. Thus, for certain and valid initial values of $v_{\min}$ and $v_{\max}$, and from Eq. (9), the values of parameters e and f are calculated in the following way:

$$e = \frac{v_{\min} - \xi v_{\max}}{1 - \xi}; \quad (10a)$$

$$f = \frac{R(v_{\min} - e)^{\nu+1}}{\nu(v_{\min} - b)^2}; \quad (10b)$$

$$\text{where,} \quad \xi = \left(\frac{v_{\min} - b}{v_{\max} - b} \right)^{2/(\nu+1)}. \quad (10c)$$

To find the values of $v_{\min}$ and $v_{\max}$ (equivalent to e and f) some initial values are proposed, and then they are modified as the solution of $T_t(v_{\min}, v_{\max}) = T_t^{(\exp)}$, where T_t is the

TABLE I. Substances data used to anchor equation of state. Pressure P_c, molar volume v_c, and temperature T_c correspond to liquid-vapor critical point. Acentric factor ω is related to saturate vapor pressure at temperature $0.7\,T_c$. T_b is the boiling point temperature, and T_t is the triple point temperature. Estimated data are shown in bold format.

| No. | Substance | CAS | P_c | v_c | T_c | ω | T_b | T_t |
			bar	cm^3/mol	Kelvin		Kelvin	Kelvin
	Alcohols							
1	1-Dodecanol[a,j]	112-53-8	19.9	**716**	719.4	0.666	534.2	296.95
2	1-Propanol[a,b]	71-23-8	52	218	536.9	0.6209	370.3	148.75
3	Ethanol[a,b]	64-17-5	63	168	514	0.6436	351.5	159.0

No.	Substance	CAS	P_c	v_c	T_c	ω	T_b	T_t
			bar	cm^3/mol	Kelvin		Kelvin	Kelvin
4	Isopropanol[a,g]	67-63-0	49	222	509	0.6689	355.5	184.9
5	Phenol[a,j]	108-95-2	59.3	229	694.3	0.426	455	314.06
6	tert-Butanol [a,g]	75-65-0	39.72	275	506.2	0.6158	355.6	298.96
	Aldehydes							
7	Acetaldehyde[b,j]	75-07-0	55.7	154	466	0.2625	294.15	**149.78**
8	Butanal[a,j]	123-72-8	43.2	258	537.1	0.277	348	176.28
	Alkenes							
9	1,2-Butadiene[a,g]	590-19-2	45	219	444	0.2509	284	136.92
10	1-Butene[a,b]	106-98-9	40.2	241	419.5	0.1845	266.91	87.8
11	1-Heptene[a,g]	592-76-7	29.2	409	537.3	0.331	367	154.3
12	1-Hexene[a,g]	592-41-6	31.4	354	504.03	0.28	336.63	133.39
13	1-Octene[a,g]	111-66-0	25.5	472	566.6	0.3747	394.44	171.46
14	1-Pentene[a,g]	109-67-1	35.6	298.4	464.8	0.233	304	108.01
15	3-Methyl-1-butene[a,j]	563-45-1	35.3	304.9	452.7	0.21	293	104.71
16	Cis-2-Butene[b]	590-18-1	42.1	234.1	435.5	0.2019	276.87	134.26
17	Cis-2-pentene[a,j]	627-20-3	36.9	302.1	475	0.241	309.8	121.78
18	Ethylene[a,b]	74-85-1	50.6	131	282.5	0.0863	169	104
19	Isoprene[a,g]	78-79-5	37.4	266	483.3	0.164	307.22	127.27
20	Propadiene[a,g]	463-49-0	52.5	162	393.15	0.1594	240	136.59
21	Propylene[b,g]	115-07-1	46.126	185	364.85	0.1376	225.45	87.89
22	Trans-2-Butene[a,b]	624-64-6	41	238	428.6	0.2176	274.03	167.62
23	Trans-2-pentene[a,j]	646-04-8	36.54	302.1	475.37	0.237	309.4	132.93
	Alkyl amines							
24	Dimethyl ether[b]	115-10-6	53.7	170	400.1	0.2002	248.31	131.65
25	Methylamine[a,b]	74-89-5	74.6	138.5	430.05	0.2814	266.82	179.69
	Alkyl halides							
26	1,1,1-Trifluoroethane[a,j]	420-46-2	37.639	195	345.86	0.261	226	161.82
27	1,1,2,2-Tetra-chloroethane[a,g]	79-34-5	40.9	325	645	0.2592	418.25	230.8
28	1,1-Dichloroethane[a,j]	75-34-3	50.61	240	523.4	0.234	330.5	176.18
29	1-Chloro-1,1-difluoroethane[a,j]	75-68-3	40.48	225	410.2	0.231	263.2	142.71
30	Carbon Tetrachloride[a,j]	56-23-5	44.93	276	556.36	0.193	349.8	249
31	Chloroform[a,b]	67-66-3	54.72	239	536.4	0.2219	334.33	209.61
32	Ethyl-Chloride[a,g]	75-00-3	52.405	200	460.35	0.1905	289	134.82
33	Ethylene Dichloride[a,g]	107-06-2	53.8	220	561.6	0.2876	356.7	237.6
34	Fluorocarbon-11[a,g]	75-69-4	44.076	248	471.2	0.1837	296.97	162.6
35	Fluorocarbon-13[a,g]	75-72-9	39.46	180.28	301.96	0.18	191.74	92
36	Fluorocarbon-14[a,g]	75-73-0	37.389	140	227.5	0.1855	145.09	89.4
37	Fluorocarbon-22[a,g]	75-45-6	49.71	166	369.3	0.2192	232.32	115.76
38	Fluorocarbon-23[a,g]	75-46-7	48.362	133.3	298.89	0.2672	190.99	117.97
39	Fluorocarbon-113[a,g]	76-13-1	34.146	325.31	487.25	0.2552	320.75	236.55
40	Fluorocarbon-114[a,g]	76-14-2	32.627	293.68	418.85	0.252	276.92	179
41	Fluorocarbon-116[a,g]	76-16-4	30.42	224	292.8	0.2452	195	173.08
42	Methyl Chloride[a,g]	74-87-3	67.144	139	416	0.1529	247	175.43
43	Methyl fluoride[a,h,j]	593-53-3	58.7	113	317.4	0.198	195	129.8
44	Methyl-chloroform[a,g]	71-55-6	42.962	281	545	0.2157	347.23	243.13

No.	Substance	CAS	P_c	v_c	T_c	ω	T_b	T_t
			bar	cm^3/mol	Kelvin		Kelvin	Kelvin
45	Octafluorocyclobutane[a,j]	115-25-3	27.84	325	388.46	0.356	267.3	232.96
46	Pentafluoroethyl chloride[a,j]	76-15-3	31.2	252	352.94	0.251	235	173.71
47	Perchloro-ethylene[a,g]	127-18-4	44.9	248	620	0.221	394.2	250.81
48	Vinyl Chloride[a,g]	75-01-4	56.7	179	432	0.1048	259.35	119.31
49	Vinylidene Chloride[a,g]	75-35-4	46.8	219	489	0.179	304.2	150.59
	Alkyl silanes							
50	Tetramethylsilane[a,j]	75-76-3	28.21	362	448.64	0.224	299.7	172
	Alkyl siloxane							
51	Decamethyl-cyclopentasiloxane[a,i]	541-02-6	10.35	1287	617.4	0.6658	484.1	226
52	Octamethyl-cyclotetrasiloxane[a,j]	556-67-2	13.2	1005	585.7	0.589	448	290.25
	Alkynes							
53	2-Butyne[a,j]	503-17-3	**48.7**	**221**	**473.2**	0.239	300	240.8
54	Acetylene[a,b]	74-86-2	61.38	112.2	308.3	0.1912	189	192.4
55	Methylacetylene[a,g]	74-99-7	56.3	163.5	402.4	0.2161	250	168.5
	Amines							
56	Ethylamine[b]	75-04-7	56.2	**207**	456.15	0.2848	289.73	**192.15**
57	tert-butylamine[a,j]	75-64-9	38.4	293	483.9	0.275	318	206.19
	Aromatic amines							
58	Aniline[a,j]	62-53-3	53.1	**270**	698.8	0.378	457	267.13
	Aromatic hydrocarbons							
59	1,2,3,4-Tetrahydro-naphthalene[a,j]	119-64-2	37	408	720	0.335	481	237.34
60	Benzene[a,b]	71-43-2	48.9	250	562	0.2103	353.24	278.5
61	Cumene[a,b]	98-82-8	32.09	434	631	0.3274	425.56	177.13
62	Ethylbenzene[a,b]	100-41-4	36.4	374	617	0.3035	409.35	178.15
63	Naphthalene[a,b,c]	91-20-3	41	407	748	0.3020	490	353.15
64	p-Cymene[a,j]	99-87-6	28	497	652	0.374	450	204.2
65	Styrene[a,b]	100-42-5	**38.4**	352	**636**	0.2971	418.31	242.47
66	Toluene[a,b]	108-88-3	41	316	593	0.2640	383.78	178.15
	Brominated hydrocarbons							
67	Ethylene Dibromide[a,g]	106-93-4	54.769	261.57	650.15	0.2067	404.51	283
	Carbonyl compounds							
68	Methylal[a,j]	109-87-5	39.5	213	480.6	0.29	315.3	168.03
69	Phosgene[a,j]	75-44-5	56.74	190.2	455	0.201	280.71	145.37
	Carboxylic acids							
70	Benzoic acid[a,j]	65-85-0	44.7	344	751	0.603	522.2	395.52
71	Butanoic acid[a,j]	107-92-6	40.64	291.7	615.2	0.681	436	267.97
72	Dodecanoic acid[a,j]	143-07-7	18.678	**705**	743.43	0.88	571	316.98
73	Octanoic acid[a,j]	124-07-2	28.69	499	693	0.771	510	289.66
74	Propanoic acid[a,j]	79-09-4	46.68	233	600.81	0.575	414	252.65
75	Tridecanoic acid[a,j]	638-53-9	17.489	**758**	754.01	0.904	585.25	315.01
	Cyclic alkenes							
76	2-Norbornene[a,j]	498-66-8	48.6	337	590	0.159	369.2	319.5
	Cyclic amines							
77	Pyrrolidine[a,j]	123-75-1	57	249	568.6	0.267	360	215.31

No.	Substance	CAS	P_c	v_c	T_c	ω	T_b	T_t
			bar	cm^3/mol	Kelvin		Kelvin	Kelvin
	Dialkyl ethers							
78	Diethyl ether[a,b]	60-29-7	36.4	280	466.7	0.2811	307.58	156.92
79	Methyl butyl ether[a,j]	628-28-4	33.71	329	512.8	0.313	344.2	157.48
80	Methyl propyl ether[a,j]	557-17-5	38.01	276	476.3	0.277	311.7	133.97
	Dialkyl sulfides							
81	Diethyl sulfide[a,j]	352-93-2	39.6	318	557	0.29	365	169.21
	Elements							
82	Argon[a,f]	7440-37-1	48.979	74.57	150.86	-0.0022	87.28	83.8
83	Nitrogen[b]	7727-37-9	34.0	89.21	126.2	0.03772	77.344	63.149
	Esters							
84	Ethyl acetate[a,j]	141-78-6	38.82	286	523.3	0.366	350.2	189.3
85	Methyl acetate[a,j]	79-20-9	47.5	228	506.55	0.331	330	174.9
	Halo aromatic compound							
86	Hexafluorobenzene[a,j]	392-56-3	33	335.1	517	0.395	353.4	278.3
	Heterocyclic compounds							
87	1,4-Dioxane[a,j]	123-91-1	54.716	239	587.3	0.28	374.3	284.1
88	Pyridine[a,j]	110-86-1	56.6	253	619	0.239	388.5	231.48
89	Tetrahydrofuran[a,j]	109-99-9	51.9	225	540.2	0.226	339	164.76
	Hydrides							
90	Ammonia[b]	7664-41-7	112.8	72.47	405.65	0.2526	239.72	195.4
91	Hydrogen sulfide[b]	7783-06-04	89.629	98.5	373.53	0.0942	212.8	187.68
92	Water[b]	7732-18-5	220.64	55.947	647.1	0.3449	373.15	273.16
	Ketones							
93	2-Hexanone[a,j]	591-78-6	33.2	378	586.6	0.385	400	217.69
94	2-Octanone[a,j]	111-13-7	**26.4**	497	632.7	0.455	446	252.79
95	3-Pentanone[a,j]	96-22-0	37.29	336	561.5	0.345	375	234.16
96	Acetone[a,b]	67-64-1	47	208.92	508.2	0.3069	329.28	178.5
97	Methyl ethyl ketone[a,b]	78-93-3	42.07	267	536.7	0.3244	352.73	186.5
98	Methyl-isopropyl ketone[a,j]	563-80-4	38	310	553.1	0.321	367	180.01
99	Methyl-propyl ketone[a,j]	107-87-9	36.94	301	561.1	0.343	375	196.31
100	Octamethyltrisiloxane[i]	107-51-7	14.15	882	564.1	0.531	423.4	187.2
	Monocyclic heteroarenes							
101	Furan[a,j]	110-00-9	53.2	219	490.2	0.202	304.7	187.54
	Mono-halo benzenes							
102	Bromobenzene[a,j]	108-86-1	45.19	324	670.15	0.251	429.1	242.42
103	Chlorobenzene[a,j]	108-90-7	45.191	308	632.65	0.25	404.9	227.9
104	Fluorobenzene[a,j]	462-06-6	45.505	269	560.1	0.247	358	230.92
105	Iodobenzene[a,j]	591-50-4	45.19	351	721.15	0.247	461.4	241.8
	Nitriles							
106	Acetonitrile[a,j]	75-05-8	48.7	173	545	0.338	354.8	229.32
	Nitrogen compounds							
107	Ethanethiol[a,j]	75-08-1	54.9	207	499	0.188	309	125.25
	Oxides							
108	Butylene Oxide[a,j]	106-88-7	**43.9**	**258**	**526**	0.235	336.5	143.87

No.	Substance	CAS	P_c	v_c	T_c	ω	T_b	T_t
			bar	cm^3/mol	Kelvin		Kelvin	Kelvin
	Methyl siloxanes							
109	Ethylene Oxide[a,g]	75-21-8	72.33	140.3	468.9	0.1979	285	160.65
110	Propylene Oxide[a,g]	75-56-9	49.244	186	482.25	0.271	307.05	161.22
	Sulfides							
111	Carbon disulfide[a,j]	75-15-0	79	160	552	0.111	319.2	161.11
112	Carbonyl sulfide[a,j]	463-58-1	63.49	135.1	378.8	0.097	223	134.31
113	Dimethyl sulfide[a,j]	75-18-3	55.3	201	503	0.194	311	174.85
	Tio compounds							
114	Methanethiol[a,j]	74-93-1	72.3	145	469.9	0.158	279.1	150.14
115	Thiophene[a,j]	110-02-1	57	220	579.4	0.197	357.3	235.02

a: NIST [15]; *b*: DIPPR [16]; *c*: DDB [17]; *d*: Poling, [18]; *e*: Sedunov, [19]; *f*: Velasco, [20]; *g*: Gallant, [21]; *h*: Nicola, [22]; *i*: Colonna, [23, 24]; *j*: Yaws, [25].

is the triple point temperature predicted by the Non-CEoS as a function of $v_{\min}$ and $v_{\max}$, and $T_t^{(\exp)}$ is the experimental triple point temperature of the substance. This procedure enables us to find the parameters e and f, and in this way, it defines the Non-CEoS for a particular substance. The parameter f has very small values, and that indicates that the contribution of the last term in Eq. (1a) is relevant only when the molar volume is very close to b.

3.3. Phase coexistence

Using the Non-CEoS defined in previous subsections, it is possible to find the equilibrium coexistence states using an excess thermodynamic function. In this work, the substance fugacity is used to determine the solid-liquid, the solid-vapor, and the liquid-vapor coexistences and is defined through the Helmholtz excess free energy ΔA that is written as

$$\Delta A(n,v,T) = \Delta A_0(n,v,T)$$
$$- \frac{nfT}{(\nu-1)(v-e)^{\nu-1}}; \quad (11a)$$

$$\Delta A_0(n,v,T) = n\left(RT \ln\left(\frac{v}{v-b}\right) \right.$$
$$\left. + \frac{a(T)}{c-d}\ln\left(\frac{v-c}{v-d}\right) \right), \quad (11b)$$

where n is the mole number and ΔA_0 is the Helmholtz excess free energy of the cubic equation of state. The fugacity coefficient ϕ is calculated from ΔA in the following way

$$\ln(Z\phi) = \frac{1}{RT}\left(\frac{\partial \Delta A}{\partial n}\right), \quad (12)$$

where $Z = Pv/RT$ is the fluid compressibility.

Substance fugacity f is used to determine the solid-liquid, the solid-vapor, and the liquid-vapor coexistences, because is a positive function (f > 0).

Solid-liquid$_1$ phase coexistence appears under the following conditions: the iso-fugacity criterion is fulfilled (f$^{(s)}$ = f$^{(l_1)}$), and the pressure at each phase reaches a common value ($P^{(sl_1)}$). In a similar way, liquid$_2$-vapor phase coexistence is found under the following conditions: the temperature is below the liquid-vapor critical temperature and over the triple point temperature, the iso-fugacity criterion is fulfilled (f$^{(l_2)}$ = f$^{(v)}$), and pressure reaches a common value $P^{(l_2v)}$. Liquid$_1$ phase is different to liquid$_2$ phase because $v_{l_1} < v_{l_2}$ and $P^{(sl_1)} > P^{(l_2v)}$. However, at the triple point temperature, $v_{l_1} = v_{l_2}$ and $P^{(sl_1)} = P^{(l_2v)}$ are fulfilled, *i.e.* the liquid$_1$ and the liquid$_2$ phases are the same liquid phase.

In the last third case, solid-vapor coexistence exists if the temperature is below the triple point temperature. In this case, f$^{(s)}$ = f$^{(v)}$ and $P^{(sv)} < P_t$ (where P_t is the common value of pressure at the triple point, which was predicted using the Non-CEoS).

TABLE II. Database of parameters for pure substances included in this study.

No.	Substance	b	c	d	e	f	λ	ε/R	Error
		cm^3/mol	cm^3/mol	cm^3/mol	cm^3/mol	u^*		Kelvin	%
	Alcohols								
1	1-Dodecanol	106.259	38.2203	-1002.22	96.6820	1.69148 [14]	1.91318	877.613	0.00
2	1-Propanol	89.4599	84.1686	-378.098	88.5921	4.54712 [02]	1.82361	414.648	1.67
3	Ethanol	55.4330	49.1444	-278.933	54.2712	1.06965 [04]	1.78541	473.742	1.96
4	Isopropanol	42.1007	19.7526	-259.540	38.3314	4.54262 [09]	1.71191	642.622	3.19

TABLE II. Database of parameters for pure substances included in this study.

No.	Substance	b cm^3/mol	c cm^3/mol	d cm^3/mol	e cm^3/mol	f u^*	λ	ε/R Kelvin	Error %
	Alcohols								
5	Phenol	87.9528	82.6644	-457.097	84.6185	1.29874 [09]	2.24894	354.838	0.00
6	tert-Butanol	75.6395	58.8250	-369.078	68.8813	4.04213 [12]	1.70821	535.680	0.01
	Aldehydes								
7	Acetaldehyde	41.9828	36.2723	-311.864	39.7951	1.16205 [07]	2.69413	197.355	0.01
8	Butanal	95.1014	87.3180	-442.147	92.0627	4.44347 [08]	2.38439	224.021	0.00
	Alkenes								
9	1,2-Butadiene	94.4402	89.1025	-346.904	92.5157	3.11923 [06]	2.42411	149.447	0.00
10	1-Butene	87.0965	76.4679	-308.206	85.5117	3.22086 [05]	2.23673	182.272	0.00
11	1-Heptene	76.6898	27.0665	-406.676	69.1392	9.50764 [12]	1.93644	498.370	6.78
12	1-Hexene	140.842	130.242	-543.716	137.820	3.73412 [08]	2.24030	220.516	0.02
13	1-Octene	191.950	180.006	-803.399	187.773	1.30556 [10]	2.15939	283.082	0.01
14	1-Pentene	95.5578	78.8561	-364.766	93.1646	3.10592 [07]	2.06973	267.085	2.06
15	3-Methyl-1-butene	134.046	125.465	-411.089	131.978	6.11339 [06]	2.32153	155.289	0.00
16	Cis-2-Butene	89.9933	81.6984	-329.475	87.1108	2.50507 [08]	2.33182	168.392	0.00
17	Cis-2-Pentene	115.393	103.182	-382.566	112.723	9.77054 [07]	2.09232	234.852	0.01
18	Ethylene	51.2221	46.2477	-168.667	47.9086	1.02485 [09]	2.70773	68.1916	0.00
19	Isoprene	79.7165	67.7704	-423.921	76.4063	1.09543 [09]	2.60993	180.822	0.01
20	Propadiene	66.0640	61.7737	-264.473	63.2227	1.88175 [08]	2.88766	86.8453	0.00
21	Propylene	67.7493	59.5156	-229.928	65.7060	5.09648 [06]	2.35258	135.076	0.00
22	Trans-2-Butene	100.011	93.2699	-348.447	95.4817	3.24612 [10]	2.39029	146.891	0.00
23	Trans-2-pentene	125.282	115.849	-416.509	122.254	3.90006 [08]	2.22963	193.132	0.00
	Alkyl amines								
24	Dimethyl ether	68.5617	63.1217	-241.166	65.9782	6.80488 [07]	2.37384	142.244	0.00
25	Methylamine	59.2255	54.8417	-177.875	56.6501	6.98753 [07]	2.04756	207.559	0.00
	Alkyl halides								
26	1,1,1-Trifluoroethane	71.7874	65.4783	-316.272	67.2126	4.08860 [10]	2.34636	146.380	0.00
27	1,1,2,2-Tetra-chloroethane	110.269	98.7490	-545.224	104.743	2.99547 [11]	2.38647	283.604	0.00
28	1,1-Dichloroethane	97.7992	89.9383	-327.606	94.5856	8.11025 [08]	2.21687	217.985	0.01
29	1-Chloro-1,1-difluoroethane	98.9709	93.7979	-360.307	96.1057	2.24099 [08]	2.54592	119.363	0.01
30	Carbon Tetrachloride	111.488	103.295	-416.349	105.007	1.79785 [12]	2.50950	175.155	0.01
31	Chloroform	109.949	103.695	-311.680	106.696	1.01984 [09]	2.27039	185.419	0.00
32	Ethyl-Chloride	45.6400	25.2446	-201.262	42.2946	1.20728 [09]	2.07340	317.237	0.00
33	Ethylene Dichloride	96.7939	92.4313	-397.145	93.1547	2.92065 [09]	2.55142	173.879	0.00
34	Fluorocarbon-11	92.9212	82.7737	-320.564	88.1255	6.03908 [10]	2.26145	193.993	0.00
35	Fluorocarbon-13	73.7157	67.5887	-236.713	71.1223	6.89405 [07]	2.33463	106.892	0.00
36	Fluorocarbon-14	61.3516	57.7414	-205.002	58.9225	3.68692 [07]	2.57059	61.5552	0.00
37	Fluorocarbon-22	64.9947	59.6007	-244.285	62.6413	2.35645 [07]	2.35030	140.815	0.00
38	Fluorocarbon-23	54.2442	50.7243	-218.925	51.8429	2.97360 [07]	2.38813	112.036	0.00
39	Fluorocarbon-113	133.805	123.974	-468.291	124.561	8.14008 [13]	2.23266	202.806	0.01
40	Fluorocarbon-114	113.455	102.828	-402.616	106.193	5.77790 [12]	2.15805	196.034	0.00
41	Fluorocarbon-116	69.3353	54.9751	-252.599	63.4768	9.16136 [11]	1.98157	186.966	0.00

No.	Substance	b cm^3/mol	c cm^3/mol	d cm^3/mol	e cm^3/mol	f u^*	λ	ε/R Kelvin	Error %
42	Methyl Chloride	60.8552	57.5153	-216.505	57.9627	2.41820 [08]	2.93692	80.1111	0.01
43	Methyl fluoride	41.0220	37.4162	-189.015	38.5953	3.64036 [07]	2.61762	103.013	0.01
44	Methyl-chloroform	106.551	96.9037	-415.198	99.6345	3.69357 [12]	2.35424	212.797	0.01
45	Octafluorocyclobutane	132.332	121.543	-439.019	119.344	3.53210 [15]	1.94610	227.922	0.09
46	Pentafluoroethyl chloride	65.4893	46.4315	-296.469	59.4958	1.08858 [12]	2.04486	241.109	0.00
47	Vinyl Chloride	59.6605	49.5496	-205.694	56.6245	3.92999 [08]	2.33910	169.698	0.00
48	Perchloro-ethylene	56.7095	45.8883	-506.699	50.9085	5.69346 [11]	2.89683	252.517	0.00
49	Vinylidene Chloride	85.0767	79.0791	-375.912	82.3887	1.15339 [08]	2.83027	122.676	0.00
	Alkyl silanes								
50	Tetramethylsilane	80.5486	42.1925	-359.040	73.2453	8.54569 [12]	2.01528	335.925	0.00
	Alkyl siloxane								
51	Decamethyl-cyclopentasiloxane	367.901	294.371	-1761.04	354.791	4.30891 [15]	1.67370	673.386	0.00
52	Octamethyl-cyclotetrasiloxane	437.008	411.666	-1522.91	418.004	2.26605 [17]	1.75470	451.374	0.01
	Alkynes								
53	2-Butyne	90.8890	84.2541	-320.030	85.1092	5.33931 [11]	2.28807	184.898	0.01
54	Acetylene	39.9252	35.3173	-156.263	36.4821	2.34211 [09]	2.32643	127.113	0.10
55	Methylacetylene	66.7030	61.5949	-232.069	63.4242	1.02058 [09]	2.32681	149.695	0.00
	Amines								
56	Ethylamine	98.1782	92.6078	-244.634	95.8987	2.36089 [07]	2.00199	207.914	0.00
57	tert-butylamine	98.5496	82.9128	-350.216	91.0570	8.97341 [12]	1.96842	302.013	0.00
	Aromatic amines								
58	Aniline	103.077	95.8251	-483.093	100.029	4.97729 [08]	2.20214	357.301	0.00
	Aromatic hydrocarbons								
59	1,2,3,4-Tetrahydro-naphthalene	136.818	121.192	-651.961	131.610	1.56089 [11]	2.14407	411.149	0.00
60	Benzene	91.4136	82.5509	-379.534	83.7074	1.21110 [13]	2.40075	217.450	0.01
61	Cumene	180.867	169.385	-683.164	178.766	9.66457 [06]	2.17247	292.521	0.01
62	Ethylbenzene	141.830	129.147	-558.326	139.190	1.07451 [08]	2.13693	313.138	0.00
63	Naphthalene	175.830	165.817	-637.531	166.703	7.13574 [13]	2.24624	307.452	0.01
64	p-Cymene	202.249	189.520	-836.854	197.593	4.34145 [10]	2.14756	328.477	0.00
65	Styrene	147.051	138.760	-606.895	142.231	6.90432 [10]	2.38860	239.513	0.00
66	Toluene	139.507	132.644	-526.708	136.363	5.79219 [08]	2.49052	186.944	0.00
	Brominated hydrocarbons								
67	Ethylene Dibromide	93.2478	83.0062	-378.536	85.7219	8.58397 [12]	2.33333	270.555	0.01
	Carbonyl compounds								
68	Methylal	48.8966	40.3438	-461.870	45.2816	2.91331 [09]	2.77046	225.987	0.01
69	Phosgene	83.5071	78.1702	-257.818	80.9367	6.34346 [07]	2.36188	149.387	0.01
	Carboxylic acids								
70	Benzoic acid	95.6588	78.3815	-538.946	86.4035	9.94437 [13]	1.81483	726.439	0.01
	Cyclic alkenes								
71	Butanoic acid	91.3801	81.5212	-556.429	86.7567	4.02808 [10]	1.86876	559.183	0.00
72	Dodecanoic acid	195.108	172.307	-1561.80	187.348	1.30092 [13]	1.85730	791.282	0.00
73	Octanoic acid	197.780	185.320	-894.440	193.721	1.15608 [10]	1.71848	643.375	0.00
74	Propanoic acid	87.3204	82.7237	-541.185	84.6482	1.02098 [08]	2.17674	369.054	0.01
75	Tridecanoic acid	278.465	264.034	-1853.19	272.105	1.33699 [12]	1.86654	697.040	0.00
76	2-Norbornene	120.632	90.2076	-209.210	109.830	7.03544 [14]	1.74486	391.264	0.00

No.	Substance	b cm^3/mol	c cm^3/mol	d cm^3/mol	e cm^3/mol	f u^*	λ	ε/R Kelvin	Error %
	Cyclic amines								
77	Pyrrolidine	103.263	93.5045	-279.173	98.8216	2.71342^{10}	1.93807	307.156	0.00
	Dialkyl ethers								
78	Diethyl ether	109.484	100.966	-436.484	105.538	6.94043^{09}	2.25192	205.721	0.01
79	Methyl butyl ether	87.3617	65.8423	-431.010	83.0311	2.08036^{10}	2.02729	366.938	0.01
80	Methyl propyl ether	122.449	116.407	-452.735	121.024	1.33149^{05}	2.41683	160.965	0.01
	Dialkyl sulfides								
81	Diethyl sulfide	135.462	126.983	-477.930	132.359	5.21908^{08}	2.21360	235.769	0.00
	Elements								
82	Argon	27.1282	23.3369	-82.8488	24.7496	4.07341^{07}	2.93693	28.7353	0.18
83	Nitrogen	32.9449	28.6873	-102.616	29.8623	5.95905^{08}	2.71622	30.0625	0.03
	Esters								
84	Ethyl acetate	117.631	110.635	-491.071	114.044	2.47766^{09}	2.19277	250.080	0.00
85	Methyl acetate	96.1169	90.7904	-389.580	93.6885	3.66794^{07}	2.28118	213.252	0.01
	Halo aromatic compound								
86	Hexafluorobenzene	132.449	123.127	-552.877	123.727	4.71836^{13}	2.07709	287.493	0.01
	Heterocyclic compounds								
87	1,4-Dioxane	84.9312	75.1859	-335.568	77.2707	1.06223^{13}	2.11115	314.291	0.01
88	Pyridine	95.3037	85.1821	-330.789	90.4530	7.14931^{10}	2.12937	299.598	0.01
89	Tetrahydrofuran	86.1335	79.1296	-355.673	83.1458	3.25575^{08}	2.43142	198.678	0.00
	Hydrides								
90	Hydrogen sulfide	37.3355	33.1785	-121.520	33.4892	5.77290^{09}	2.54485	107.861	0.04
91	Ammonia	26.8405	24.8563	-133.291	25.0874	1.02883^{06}	2.59408	139.929	0.01
92	Water	22.5034	21.4350	-120.654	21.9810	2.16596^{00}	2.62190	222.637	0.00
	Ketones								
93	2-Hexanone	141.043	128.903	-605.002	135.503	2.95078^{11}	2.05568	344.598	0.00
94	2-Octanone	94.0948	49.7117	-645.445	84.6883	1.23119^{14}	1.95683	618.070	0.00
95	3-Pentanone	151.475	144.214	-539.654	146.131	1.94922^{11}	2.19469	240.705	0.00
96	Acetone	72.9985	67.2458	-412.515	70.4281	7.17346^{07}	2.51677	207.439	0.00
97	Methyl ethyl ketone	109.576	103.257	-472.536	106.294	9.29351^{08}	2.33939	219.932	0.00
98	Methyl-isopropyl ketone	117.310	107.816	-505.319	113.890	1.57816^{09}	2.20526	270.407	0.00
99	Methyl-propyl ketone	110.383	102.354	-572.664	106.866	2.18667^{09}	2.36307	254.615	0.01
	Methyl siloxanes								
100	Octamethyltrisiloxane	229.677	164.904	-1063.21	218.515	6.91493^{14}	1.72918	579.425	2.03
	Monocyclic heteroarenes								
101	Furan	93.3878	86.6247	-289.132	89.1892	1.41726^{10}	2.29406	176.338	0.00
	Mono-halo benzenes								
102	Bromobenzene	129.009	119.593	-509.606	124.486	3.57177^{10}	2.35903	258.269	0.00
103	Chlorobenzene	124.730	115.995	-480.706	121.913	2.47174^{08}	2.35882	239.574	0.00
104	Fluorobenzene	106.617	98.6983	-421.706	101.457	1.45236^{11}	2.36434	214.983	0.01
105	Iodobenzene	138.241	127.533	-539.612	133.592	4.62795^{10}	2.33127	286.056	0.01
	Nitriles								
106	Acetonitrile	37.1375	31.9311	-480.538	33.2929	5.36653^{09}	3.17150	222.787	0.00
	Nitrogen compounds								
107	Ethanethiol	72.9618	63.7081	-271.393	70.8190	8.59137^{06}	2.25362	219.338	0.00

No.	Substance	b	c	d	e	f	λ	ε/R	Error
		cm^3/mol	cm^3/mol	cm^3/mol	cm^3/mol	u^*		Kelvin	%
	Oxides								
108	Butylene Oxide	93.6088	84.5819	-400.412	90.8401	$1.44570^{\,08}$	2.35366	218.381	0.01
109	Ethylene Oxide	42.1808	34.7944	-195.085	39.2386	$2.85145^{\,08}$	2.29578	229.101	0.00
110	Propylene Oxide	71.5496	67.6066	-395.398	69.4176	$8.66599^{\,06}$	2.87424	133.018	0.01
	Sulfides								
111	Carbon disulfide	62.5277	56.8933	-220.382	60.0995	$3.53013^{\,07}$	2.70631	138.221	0.01
112	Carbonyl sulfide	48.2347	42.4828	-181.483	45.1598	$4.86637^{\,08}$	2.65226	107.148	0.01
113	Dimethyl sulfide	74.3675	67.0928	-294.731	70.6049	$4.17780^{\,09}$	2.40588	188.291	0.00
	Tio compounds								
114	Methanethiol	56.9685	52.3211	-214.673	54.9625	$4.68457^{\,06}$	2.61011	134.553	0.00
115	Thiophene	81.0327	73.4849	-339.676	76.2580	$6.23326^{\,10}$	2.47880	206.248	0.00

Unit: $u^* \equiv \text{bar}\,(\text{cm}^3/\text{mol}\,)^{12}/\text{Kelvin}$ Nomenclature: $1.23456^{\,12} = 1.23456 \times 10^{12}$

4. Results and discussion

The procedure described in the previous section enables us to define the Non-CEoS for a particular substance with seven parameters $\{b, c, d, e, f, \lambda, \varepsilon\}$. Once this equation of state is defined, the $P - T$ and $P - V$ phase diagrams of a substance can be predicted. This Non-CEoS captures the main features of this type of diagrams, including the liquid-vapor critical point, the triple point, and some points from any of the different phase transitions: solid-liquid, liquid-vapor or solid-vapor.

In order to study mixtures in a future application, the Non-CEoS was applied to several substances. The adjustment of the Non-CEoS was evaluated through the agreement between the experimental data used to calculate the parameters $\{b, c, d, e, f, \lambda, \varepsilon\}$ and the values calculated with the resulting Non-CEoS once it was defined. The experimental data used to calculate the parameters mentioned in the previous paragraph are included in Table I. These data are the input information for Eqs. (1a)-(1d).

The values of pure component parameters for each of the substances included in this study are reported in Table II. These parameters make it possible to obtain a complete phase diagram (including solid, liquid and vapor phases) for each substance. The percent deviation of numerical values with respect to its corresponding reference value is in the last column in Table II. The percent deviation is calculated as follows:

$$\text{Error} = \sqrt{\frac{1}{6}\sum_{i=1}^{6} e_i^2} \times 100\% \qquad (13)$$

where $e_1 = P_c/P_c^{(\exp)} - 1$; $e_2 = v_c/v_c^{(\exp)} - 1$; $e_3 = T_c/T_c^{(\exp)} - 1$; $e_4 = \omega/\omega^{(\exp)} - 1$; $e_5 = T_b/T_b^{(\exp)} - 1$; and $e_6 = T_t/T_t^{(\exp)} - 1$.

The database reported in Table II is useful for many areas of industrial applications. As an example, some $P - T$ dia-
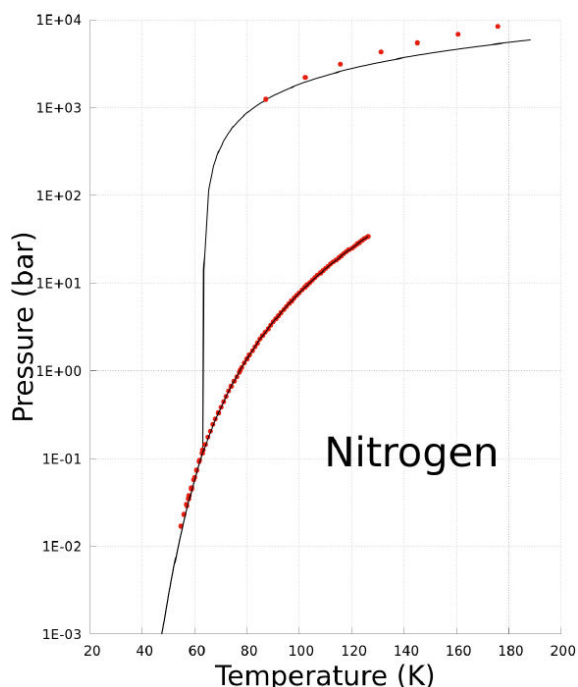

FIGURE 1. $P - T$ phase diagram of Nitrogen. Black solid-line corresponds to prediction of the Non-CEoS reported in this work. Red dots are experimental data [17, 26, 27].

grams and one $P - V$ diagram are presented in following subsections.

4.1. $P - T$ phase diagram

The coexistence states of a substance can be predicted using the Non-CEoS defined with the parameters reported in Table II. As an example, the prediction of the $P - T$, and $P - V$ phase diagrams of nitrogen are plotted in Figs. 1, and 2. In these graphs the prediction of Non-CEoS is represented with black solid-line and, for comparison, experimental data are shown with red dots.

Ammonia is another example. In Fig. 3 experimental data is compared with the prediction made with the Non-CEoS in
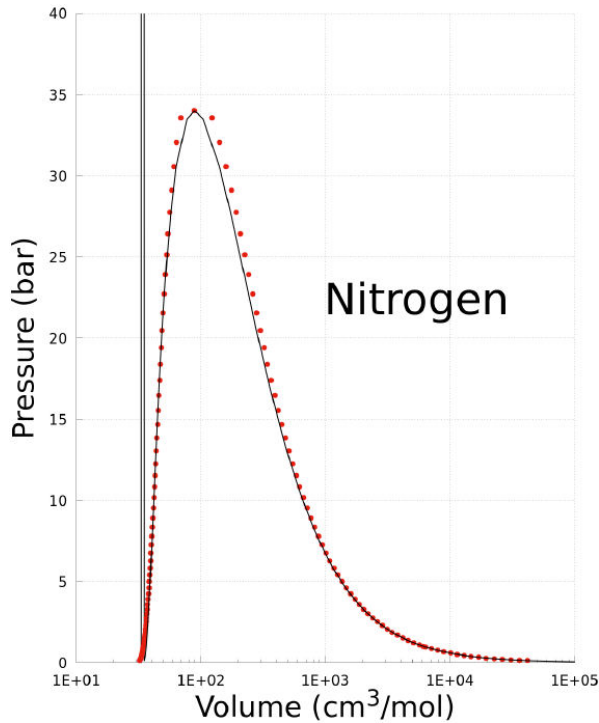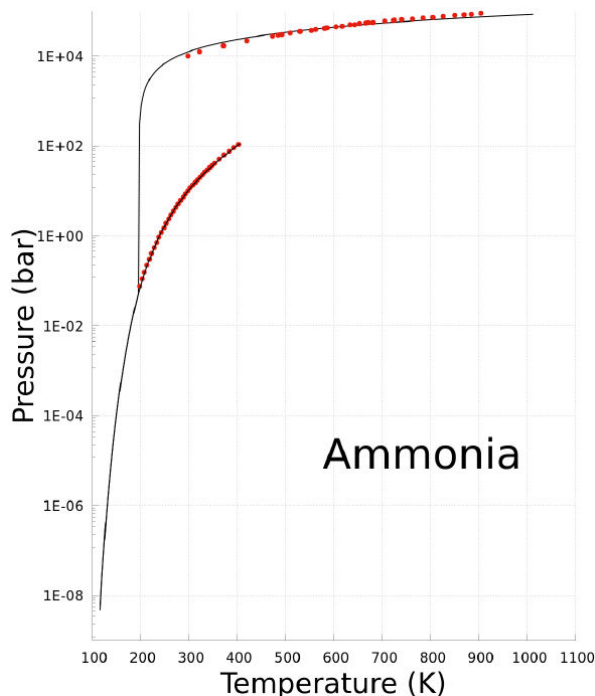
FIGURE 2. $P - V$ phase diagram of Nitrogen. Black solid-line corresponds to prediction of the Non-CEoS reported in this work. Red dots are experimental data [27].
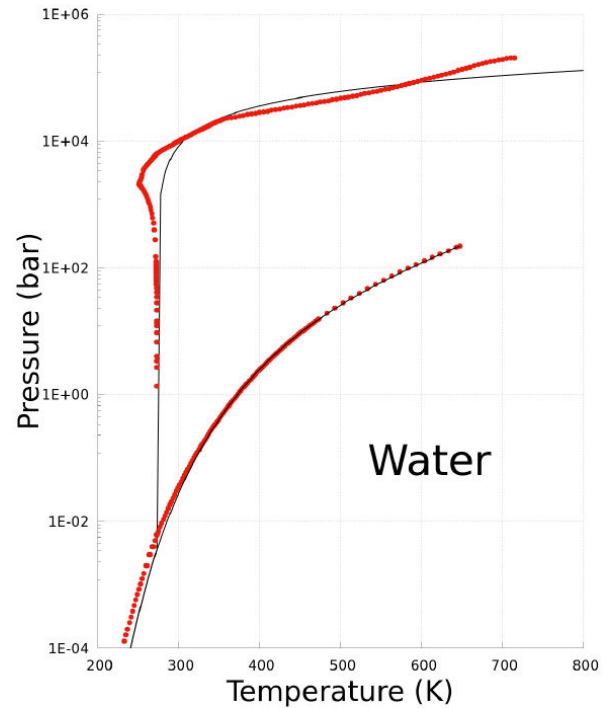

FIGURE 4. $P - T$ phase diagram of water. Black solid-line corresponds to prediction of the Non-CEoS reported in this work. Red dashed-line corresponds to IAPWS data [30, 31].

cubic equations of state can not predict, and is in agreement with the experimental data.

Thus, at least in these three examples the prediction capability of the Non-CEoS is demonstrated, but this feature is applicable to all substances in the database. A special case is that of water, that will be discussed in the following section.

4.2. The water case

Water is a special case of substance. Water molecules can be organized in several clusters with different geometries mainly because their dipole moment. Thus, there are several triple points at its phase diagram, and define several ice types. In particular, the ice-I has a solid-liquid boundary with negative slope so that the melting point decreases with pressure. This feature is due to the dipole-dipole interactions which are highly anisotropic.

On the other hand, the last term in Eq. (1a) for the Non-CEoS corresponds to very short-range interactions between the molecules, and the solid phase is formed with these interactions. However, the last term in Eq. (1a) must correspond to an isotropic potential. Under this conjecture, the resulting melting curve of ice-I, which is predicted with the Non-CEoS, must not describe a negative slope because the equation of state is isotropic. The phase diagram of water is showed at Fig. 4. The black solid-line at Fig. 4 corresponds to the prediction of Non-CEoS in this work, while the red dashed-line corresponds to the International Association for the Properties of Water and Steam (IAPWS) data [30, 31]. Clearly, the resulting phase diagram does not capture the

FIGURE 3. $P - T$ phase diagram of Ammonia. Black solid-line corresponds to prediction of the Non-CEoS reported in this work. Red dots are experimental data [28, 29].

a $P - T$ phase diagram. The prediction from the Non-CEoS includes solid-liquid and solid-vapor coexistence states that

TABLE III. Water properties.

	Results	References	Error
Critical point			
Pressure	220.0 bar	220.64 bar	-0.29%
Molar volume	55.9472 cm^3/mol	55.947 cm^3/mol	0.00%
Temperature	647.096 Kelvin	647.1 Kelvin	0.00%
Boiling point			
Pressure	1.01325 bar	1.01325 bar	0.00%
Molar volume$^{(s)}$	23.4162 cm^3/mol		
Molar volume$^{(v)}$	30328.0 cm^3/mol		
Temperature	373.151 Kelvin	373.15 Kelvin	0.00%
Melting point			
Pressure	1.01325 bar	1.01325 bar	0.00%
Molar volume$^{(s)}$	22.5297767(70) cm^3/mol		
Molar volume$^{(l)}$	22.9448(30) cm^3/mol		
Temperature	273.16(57) Kelvin	273.15 Kelvin	0.01%
Triple point			
Pressure	0.0036256 bar	0.0061173 bar	-40.7%
Molar volume$^{(s)}$	22.5297767(58) cm^3/mol		
Molar volume$^{(l)}$	22.9448(32) cm^3/mol		
Molar volume$^{(v)}$	6.26586×10^6 cm^3/mol		
Temperature	273.16(25) Kelvin	273.16 Kelvin	0.00%

(s): Saturated solid; (l): Saturated liquid; (v): Saturated vapor.

negative slope of the melting curve of ice-I. But, for the rest of the melting curve, the resulting phase diagram is in agreement with the IAPWS data for high temperatures. In the same Fig. 4, the agreement between the vaporization curve predicted with the Non-CEoS and the IAPWS data is evident. Moreover, there are a small deviations of the pressure near to the triple point and below to it, namely, the sublimation curve. In these cases, the small deviations are magnified by the log scale.

The fact that the melting and triple points of water are too close is well known. The resulting values of the pressure, the molar volume, and the temperature computed with Non-CEoS at both points are in Table III. In particular, the value of the molar volume of the saturated solid at the melting point and the triple point are extremely close to each other. In fact, both numerical values at Table III differ at the last digits between parentheses, and those digits are located at the eighth to ninth decimal positions. In other words, the pressure is sensitive to the value of the molar volume of the solid phase because there are significant changes of the value of the pressure with a extremely small changes on the molar volume. In spite of the above fact, the Non-CEoS is capable to distinguish the melting point from the triple point (see Table III).

5. Conclusions

A Non-CEoS was constructed for several substances, and the pure substance parameters are reported at Table II. The analytical expression of Non-CEoS is defined through parame-

ters $\{b, c, d, e, f, \lambda, \varepsilon\}$. In this work, the procedure to obtain these parameters using experimental data was explained. The experimental data required to define the Non-CEoS are: critical pressure P_c, critical molar volume v_c, and critical temperature T_c, acentric factor ω, boiling point temperature T_b, and the temperature T_t at the triple point; all of them are in Table I.

The Non-CEoS, described in Eqs. (1a)-(1d), predicts the solid-liquid, solid-vapor, and liquid-vapor phase coexistences of pure substances. This feature was demonstrated with the nitrogen, ammonia, and water cases, and is also valid for all the substances in Table I. Considering the example cases, a good agreement between the resulting phase diagrams predicted with the Non-CEoS and the experimental data was observed.

The adjustment of the values calculated with the Non-CEoS for the critical point, acentric factor, boiling temperature, and triple point temperature with respect to their experimental values, is observed through the error reported in the database (see Table II). For almost all substances in the database the numerical relative deviation is less than 1%.

The results for the solid-liquid coexistence (compared with experimental data) enable us to confirm that the last term in Eq. (1a) is related to short-range interactions between the molecules in the fluid. This is manifested by a big value of exponent (in this work $\nu = 12$). Thus, this term modifies the cubic equation only in a region defined by a small neighborhood close to the exclusion volume. As a consequence, the

pressure of the saturated solid phase is highly sensitive to the volume value, and therefore, the slope of the melting curve is very pronounced. Another implication of this fact is manifested on the calculation of the melting point temperature, because the difference between the melting point temperature and the triple point temperature is less than 1 Kelvin, as in the water case in Table III.

Acknowledgments

1. F. de J. Guevara-Rodríguez, Ecuación de estado cúbica para substancia pura usando los datos del segundo coeficiente del virial, *Rev. Mex. Fis. E* **61** (2015) 58.

2. D.-Y. Peng and D. B. Robinson, in *Equations of State in Engineering and Research*, edited by K. C. Chao and R. L. Robinson (American Chemical Society, New York, 1979), Chap. 10, pp. 185-195, `https://doi.org/10.1021/ba-1979-0182.ch010`.

3. E. Lang and H. Wenzel, Extension of a cubic equation of state to solids, *Fluid Ph. Equilibria* **51** (1989) 101, `https://doi.org/10.1016/0378-3812(89)80357-7`.

4. C. Secuianu, V. Feroiu, and D. Geană, Phase behavior for carbon dioxide + ethanol system: Experimental measurements and modeling with a cubic equation of state, *J. Supercrit. Fluid.* **47** (2008) 109, `https://doi.org/10.1016/j.supflu.2008.08.004`.

5. H. Wenzel and G. Schmidt, A modified van der Waals equation of state for the representation of phase equilibria between solids, liquids and gases, *Fluid Ph. Equilibria* **5** (1980) 3, `https://doi.org/10.1016/0378-3812(80)80040-9`.

6. A. Yokozeki, Analytical Equation of State for Solid-Liquid-Vapor Phases, *Int. J. Thermophys.* **24** (2003) 589, `https://doi.org/10.1023/A:1024015729095`.

7. A. Yokozeki, A simple theoretical model for condensed-phase equilibria based on a hard-sphere equation-of-state and its applications, *Appl. Energy* **81** (2005) 306, `https://doi.org/10.1016/j.apenergy.2004.07.012`.

8. F. de J. Guevara-Rodrãguez and A. Romero-Martãnez, An empirical extension for a generalized cubic equation of state, applied to a pure substance with small molecules, *Fluid Ph. Equilibria* **347** (2013) 22, `https://doi.org/10.1016/j.fluid.2013.03.011`.

9. G. Schmidt and H. Wenzel, A modified van der Waals type equation of state, *Chem. Eng. Sci.* **35** (1980) 1503, `https://doi.org/10.1016/0009-2509(80)80044-3`.

10. J. H. Lee and K.-P. Yoo, Comments on "Analytic Equation of State for Solid-Liquid-Vapor Phases" *Int. J. Thermophys.* **24** (2003) 589, *Int. J. Thermophys.* **32** (2011) 553, `https://doi.org/10.1007/s10765-011-0943-9`.

11. F. de J. Guevara-Rodríguez, A methodology to define the Cubic Equation of State of a simple fluid, *Fluid Ph. Equilibria* **307** (2011) 190, `https://doi.org/10.1016/j.fluid.2011.05.012`.

12. Y. Le Guennec, R. Privat, S. Lasala, and J. N. Jaubert, On the imperative need to use a consistent α-function for the prediction of pure-compound supercritical properties with a cubic equation of state, *Fluid Ph. Equilibria* **445** (2017) 45, `https://doi.org/10.1016/j.fluid.2017.04.015`.

13. Y. Le Guennec, S. Lasala, R. Privat, and J. N. Jaubert, A consistency test for α-functions of cubic equations of state, *Fluid Ph. Equilibria* **427** (2016) 513, `https://doi.org/10.1016/j.fluid.2016.07.026`.

14. A. Gil-Villegas, F. del Río, and A. L. Benavides, Deviations from corresponding-states behavior in the vapor-liquid equilibrium of the square-well fluid, *Fluid Ph. Equilibria* **119** (1996) 97, `https://doi.org/10.1016/0378-3812(95)02851-X`.

15. NIST, *Chemisty WebBook*, SRD 69, `https://doi.org/10.18434/T4D303`.

16. Design Institute for Physical Properties, Sample Database, `https://dippr.aiche.org/SamleDb`.

17. Dortmund Data Bank, `http://www.ddbst.com/free-data.html`.

18. B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The properties of gases and liquids*, 5th ed. (McGraw-Hill, New York, 2001), pp. A5-A19.

19. B. Sedunov and I. Brondz, *The Zigzag Progression of Melting and Triple Point Properties of n-Alkanes, n-Alcohols, n-Alkanoic Amines and n-Alkanoic Acids, Voice Publ.* **3** (2017) 1, `https://doi.org/10.4236/vp.2017.31001`.

20. S. Velasco, M. J. Santos, and J. A. White, Extended corresponding states expressions for the changes in enthalpy, compressibility factor and constant-volume heat capacity at vaporization, *J. Chem. Therm.* **85** (2015) 68, `https://doi.org/10.1016/j.jct.2015.01.011`.

21. R. W. Gallant, J. M. Railey, and C. L. Yaws, *Physical properties of hydrocarbons*, 2nd ed. (Gulf Publishing, Houston, 1984).

22. G. Di Nicola, C. Brandoni, C. Di Nicola, and G. Giuliani, Triple point measurements for alternative refrigerants, *J. Therm. Anal. Calorim.* **108** (2012) 627, `https://doi.org/10.1007/s10973-011-1944-4`.

23. P. Colonna, N. R. Nannan, A. Guardone, and E. W. Lemmon, Multiparameter equations of state for selected siloxanes, *Fluid Ph. Equilibria* **244** (2006) 193, `https://doi.org/10.1016/j.fluid.2006.04.015`.

24. P. Colonna, N. R. Nannan, and A. Guardone, Multiparameter equations of state for siloxanes, *Fluid Ph. Equilibria* **263** (2008) 115, `https://doi.org/10.1016/j.fluid.2007.10.001`.

25. C. L. Yaws, *Thermophysical properties of chemicals and hydrocarbons* (William Andrew, Norwich, 2008), pp. 4-95.

26. V. M. Cheng, W. B. Daniels, and R. K. Crawford, Melting parameters of methane and nitrogen from 0 to 10 kbar, *Phys. Rev. B* **11** (1975) 3972, `https://doi.org/10.1103/PhysRevB.11.3972`.

27. J. E. Jensen, W. A. Tuttle, R. B. Stewart, H. Brechna, and A. G. Prodell, *Brookhaven National Laboratory Report* No. BNL 10200-R, 1980.

28. S. Ninet and F. Datchi, High pressure-high temperature phase diagram for ammonia, *J. Chem. Phys.* **128** (2008) 154508, `https://doi.org/10.1063/1.2903491`.

29. *International Institute of Ammonia Refrigeration*, Ammonia Data Book, 2nd ed. (IIAR, Virginia, 2008), pp. A32-A35.

30. *International Association for the Properties of Water and Steam*, Report No. IAPWS R14-08(2011), 2011.

31. J. H. Keenan, F. G. Keyes, P. G. Hill, and J. G. Moore, Steam tables: *Thermodynamic properties of water including vapor, liquid, and solid phases* (Krieger Publishing, Malabar, 1992).