

Liquid Density Modeling of Pure Refrigerants Using Four Lattice-Hole Theory Based Equations of State

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The present study investigates the performance and relative accuracy of four lattice-hole theory based equations of state in modeling and correlating the liquid density of pure refrigerants. Following the gathering of a database of 5740 experimental liquid density datapoints of 36 pure refrigerants belonging to five different categories including CFCs, HCFCs, PFCs, HFCs and HFEs, ranging from 6×10^{-5} -500 MPa and 94-533 K, the pure component characteristic parameters of the EOSs were estimated and used in their comparative study. According to the results obtained, all the four EOSs can satisfactorily represent the liquid density of refrigerants with AARDs of only 0.654%, 0.684%, 0.798% and 0.859% for ϵ^* -Modified Sanchez-Lacombe, Simha-Somcynsky, MSS-II and Park-Kim EOSs, respectively. Also, based on a comparison with the commonly used Peng-Robinson, as well as the linear isotherm regularity (LIR) EOSs, with AARDs of 10.064% and 2.050%, respectively, in representing the liquid density data, it can be concluded that the large improvements obtained when using the lattice-hole theory based EOSs do justify the use of these more complex equations of state for modeling the volumetric properties of various pure refrigerants.

Nomenclature

A: Helmholtz free energy; a, b : Universal constants to be used in the MSS-II EOS; C : External degrees of freedom; c : Degrees of freedom of each mer; E_0 : Interaction energy between segments; k : Boltzmann constant; M : Molecular weight; N : Number of molecules; ND : Number of datapoints; P : Pressure (MPa); R : Universal gas constant; r : Number of lattice sites occupied by one molecule; s : Number of mers; T : Temperature (K); v_j : Free volume; V : Total volume of the system ($\text{cm}^3 \text{g}^{-1}$); v : Molar volume ($\text{cm}^3 \text{mol}^{-1}$); v_m : Molar volume (M^{-1}); y : Occupied lattice site fraction; Z : Compressibility factor; **Greeks**: α : Temperature dependent parameter (K^{-1}); ϵ_0 : The asymptotic value of the interaction energy (J mol^{-1}); ϵ^* : Interaction energy (J mol^{-1}); ρ : Density (kg m^{-3}); ρ_m : Molar density (M); ϕ : Partition function; Ω : Combinatorial factor; **Subscript**: *Calc.*: Calculated; *Exp.*: Experimental. **Superscript**: \sim : Reduced properties; $*$: Characteristic properties

Keywords: Liquid density, Refrigerant, Lattice-hole theory, Equation of state, Statistical thermodynamics

INTRODUCTION

The use of pure refrigerants and their mixtures as working fluids in industrial applications involving refrigerators and heat pumps is widespread. Accurate knowledge of the thermophysical properties of refrigerants, e.g. liquid density, over a wide range of pressures and temperatures is essential in proper and economical designing of refrigeration processes, as well as air conditioning and heat pumping systems. Nonetheless, direct

experimental measurement of these properties over an extended temperature and pressure range could in some cases be impractical, expensive or time consuming.

Historically, a great deal of effort has been devoted to the development of procedures for estimating and correlating the thermo-physical properties of pure components and mixtures; of which various equations of state (EOS) are of note. This particularly demonstrates the need for ascertaining the relative capabilities of prospective EOSs in representing both volumetric and equilibrium properties of refrigerants used as working fluids. Furthermore, and in order to curb the risks posed by

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stratospheric ozone depletion, the Montreal Protocol was adopted in 1987 to reduce the production and consumption of ozone depleting substances; in an effort to reduce their abundance in the atmosphere, and thereby protect the earth's fragile ozone layer [1]. Prior to the ratification of this treaty, the principal classes of chemical compounds used as refrigerants in the refrigeration industry were chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Based on the growing scientific understanding of the effects of anthropogenic emissions of these compounds, the use and production of them were effectively prohibited. Increase in stringency and participation in Montreal Protocol has drawn the attention of researchers as well as industries to possible substitutes from other classes of chemical compounds with much lower ozone depleting potential (ODP). This underlines the necessity for proper thermodynamic modeling of the thermophysical properties of the diverse variety of refrigerants currently employed; for which there seems to be a scarcity of in the published literature and hereby has been undertaken by way of four lattice-hole theory based equations of state. Additionally, to ascertain the relative accuracy of these equations of state, comparisons have been made with the results obtained from modeling the volumetric properties of pure refrigerants by using the Peng-Robinson [2], as well as the linear isotherm regularity (LIR) [3] equations of state.

METHODS

Lattice-Hole Theory Based Equations of State

It is well known that the liquid state shares the properties of both gas and solid states. In other words, liquids have been considered both as disordered solids and as very dense gases for the purpose of constructing approximate theories [4]. In doing so, the lattice model by Sanchez and Lacombe [5] and the cell model by Lennard-Jones and Devonshire [6] are of note. In these models, which are based on statistical thermodynamics, the molecules are presumed to be consisting of repeating units called segments. This framework is similar to the concept of monomer in polymer sciences; the difference being that while the latter has its roots in physical reality, molecular segments are imaginary or mathematical units. Nonetheless, the common denominator between all such theories is that they consider the movement of each liquid molecule segment to be restricted to the neighborhood of one of the lattice sites; so that, it is usual to consider only the effect of

nearest neighbors on the molecular segment within its cell [4]. In addition, it is well known that the cell model ascribes to the liquid a structure more appropriate to the solid state and hence does not yield enough entropy. Hole theory was developed from cell model by adopting the free volume concept by Eyring and Hirschfelder [7]; where free volume is defined as the space into which the center of mass of a given molecule can move under the influence of an intermolecular potential generated by neighboring segments around the center of the cell. Specifically, although volume change in the cell theory is attributed to the change of cell volume only, it is the number of holes in the hole theory that describes the major change in volume, and the change of the cell size plays a minor role [8]. By allowing for empty sites, a mixing term is added to the entropy, with the aim of correcting the aforementioned deficiency of the cell theory, whilst retaining much of the tractability of the model; the critical step here is considered to be making judicious assumptions regarding the dependence of the free volume on the number of empty sites [9]. Essentially, the salient difference between the various hole theories proposed is either in the choice of the functional form of this dependence or the combinatorial factor, which itself determines the number of arrangements of molecules according to their structure and shape. Essentially, the partition function of the hole theory, from which the actual equation of state could be derived, is composed of three parts: combinatorial term, free volume term and an energy term as in Eq. (1) [8]:

$$\phi = \Omega v_f^{CN} \exp\left(-\frac{E_0}{kT}\right) \quad (1)$$

where ϕ is the partition function, Ω is the combinatorial factor, v_f is the free volume expressing the mobility and flexibility of molecules and E_0 is the interaction energy between segments; additionally, C and N are the external degrees of freedom and the number of molecules, respectively. Following the standard procedure of statistical thermodynamics, while having determined the functional form of the first two terms of Eq. (1), one can readily derive the corresponding lattice-hole theory based equation of state using Eq. (2) [10]:

$$P = kT \left(\frac{\partial \ln \phi}{\partial V} \right)_{T,y} \quad (2)$$

and with simultaneously minimizing the Helmholtz energy as in Eq. (3):

$$\left(\frac{\partial A}{\partial y}\right)_{T,V} = 0 \quad (3)$$

here, A represents the Helmholtz free energy and y denotes the occupied lattice site fraction.

Concisely, in the hole theory, a major change in volume is explained by the number of holes, and the change in cell size plays a minor role; whilst in the cell theory, the changes in volume, as a result of changes in temperature and pressure can be only explained by the changes in the cell size [5,11,12]. Oppositely, the lattice theory stipulates that lattice size is fixed, and volume change is explained solely by the number of vacant sites [11,12].

ε^* -Modified Sanchez Lacombe equation of state.

Following the original work of Sanchez and Lacombe [5], Machida *et al.* [13] proposed a simple modification to take into account the temperature dependence of hydrogen bonding and ionic interactions. In their work a simple function in the form of the Langmuir equation was used that reduces to the original SL EOS at high temperatures; and introduces temperature dependence into the interaction energy parameter ε^* . The final form of the EOS, for which they reported large improvements over the original SL EOS in the calculation of liquid densities of polar fluids and ionic liquids, especially in the high-pressure compressed-liquid region, is represented by Eqs. ((4) and (5)):

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}(\ln(1 - \tilde{\rho}) + (1 - \frac{1}{r})\tilde{\rho}) = 0 \quad (4)$$

$$\varepsilon^*(T) = \varepsilon_0 \frac{\alpha T}{1 + \alpha T} \quad (5)$$

where

$$\tilde{T} = \frac{T}{T^*}, \quad \tilde{P} = \frac{P}{P^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*} \quad (6)$$

$$\varepsilon^* = RT^*, \quad v^* = \frac{RT^*}{P^*}, \quad r = \frac{MP^*}{RT^* \rho^*}$$

and $\varepsilon_0, v^*, r, \alpha$, are the characteristic parameters of the EOS for each pure component.

Simha-Somcynsky equation of state. In the Simha-Somcynsky (SS) hole model, the square-well approximation to the cell potential is used and non-nearest neighbor contributions to the lattice energy are also included [9,14]. This model, in addition to incorporating vacancies in the lattice sites, as was also the case in the Sanchez-Lacombe model, allows for the changes in the lattice sizes themselves

and as such is able to more accurately describe the effect of pressure changes and also changes in the free-volume. In other words, in this model the change in total volume of a system is controlled by the cooperative changes (in) the number of holes as well as the volume of a site (cell volume) [15]. The resulting coupled equation of state must be solved simultaneously with an expression that minimizes the partition function with respect to the fraction of occupied sites, Eqs. ((7) and (8)):

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{1}{1-Q} + \frac{2y}{\tilde{T}(y\tilde{V})^2} \left[\frac{1.011}{(y\tilde{V})^2} - 1.2045 \right] \quad (7)$$

$$\left(\frac{s}{3c}\right) \left[\frac{s-1}{s} + \frac{\ln(1-y)}{y} \right] = \frac{Q-(1/3)}{1-Q} + \frac{y}{6\tilde{T}(y\tilde{V})^2} \left[2.4090 - \frac{3.033}{(y\tilde{V})^2} \right] \quad (8)$$

$$Q = \frac{y}{2^{1/6}(y\tilde{V})^{1/3}} \quad (9)$$

where Q is represented by Eq. (9) and $\tilde{P}, \tilde{V}, \tilde{T}$ are the reduced pressure, volume and temperature with respect to the characteristic parameters P^*, V^*, T^* which alongside s representing the number of mers and $3c$, the degrees of freedom of each mer, constitute the fitting parameters of the EOS.

MSS-II equation of state. By introducing the perturbed hard-chain theory of Beret and Prausnitz [16] into the original Simha-Somcynsky EOS, Wang *et al.* [15] modified the free volume contribution of the SS EOS for representing the gaseous state of low molecular-weight substances. Moreover, for better description of the properties of low molecular-weight substances, two additional empirical constants were introduced into the free volume term. By the same procedure used in the derivation of the original SS EOS, the modified SS EOS, which the authors dubbed as MSS-II, for the occupied-site fraction and pressure are obtained as the coupled Eqs. ((10) and (11)):

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \left[1 - \frac{2^{-1/6}by^a}{(y\tilde{V})^{1/3}} \right]^{-1} + \frac{2y}{(y\tilde{V})^2\tilde{T}} \left[\frac{1.011}{(y\tilde{V})^2} - 1.2045 \right] + \frac{1-c}{c} \quad (10)$$

$$\frac{s}{3c} \left(\frac{s-1}{s} + \frac{\ln(1-y)}{y} \right) - \frac{2^{-1/6}aby^a(y\tilde{V})^{-1/3} - 1/3}{1 - 2^{-1/6}y^a(y\tilde{V})^{-1/3}} - \frac{y}{6(y\tilde{V})^2\tilde{T}} \left(2.409 - \frac{3.039}{(y\tilde{V})^2} \right) + \frac{1-c}{3c} = 0 \quad (11)$$

Where $a = 1.140$ and $b = 1.257$ are treated as universal constants, which were determined from 44 low molecular-weight substances and 64 polymers.

Park-Kim equation of state. By equally partitioning the hole volume into each segment of the molecule, Park and Kim [8,17] proposed a new equation of state based on hole theory; which by being unaffected by chain length, conforms to the principle of corresponding states theory. They demonstrated that the cell volume assumed by their EOS is much larger than that of the original Simha-Somcynsky model. This is mainly because more free volume is given to a segment at the same reduced temperature and pressure. With their proposed new free volume expression and following the standard procedure of statistical thermodynamics, they developed the equation of state reproduced in Eqs. ((12) and (13)):

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{(y\tilde{V})^{1/3}}{(y\tilde{V})^{1/3} - 2^{-1/6}y} + \frac{2y}{\tilde{T}} \left(\frac{1}{y\tilde{V}} \right)^2 \left[1.011 \left(\frac{1}{(y\tilde{V})} \right)^2 - 1.2045 \right] \quad (12)$$

$$\frac{s}{3c} \frac{1}{y} \left(\frac{s-1}{s} + \frac{1}{y} \ln(1-y) \right) + \frac{-\frac{2}{3y}(y\tilde{V})^{1/3}}{(y\tilde{V})^{1/3} - 2^{-1/6}y} - \frac{1}{6\tilde{T}} \left(\frac{1}{y\tilde{V}} \right)^2 (2.409 - 3.033 \left(\frac{1}{y\tilde{V}} \right)^2) = 0 \quad (13)$$

Linear Isotherm Regularity Equation of State

Despite the fact that dense fluids are complicated at the molecular level, with diverse many-body interactions, they nonetheless exhibit a number of simple regularities [18,19]. Amongst them, it is known experimentally that for many dense fluids, isotherms plotted as $(Z - 1) v_m^2$ vs. ρ_m^2 , where $Z = Pv_m/RT$ is the compressibility factor, $\rho_m = 1/v_m$ is the molar density, and v_m is the molar volume, tend to be linear. Using this regularity and by employing an effective potential of the Lennard-Jones (6-12) type, Parsafar and Mason [3] proposed a new equation of state that applies to both compressed liquids and also dense supercritical fluids, named as linear isotherm regularity (LIR) equation of state. This EOS can be written as in Eq. (14):

$$(Z - 1)v_m^2 = A(T) + B(T)\rho^2 \quad (14)$$

which can be also expressed more conveniently as a pressure explicit equation of state as in Eq. (15):

$$P = RT\rho + A(T)RT\rho^3 + B(T)RT\rho^5 \quad (15)$$

here, A and B are temperature dependent parameters giving the intercept and slope of the equation of state as represented in Eq. (14). The temperature dependence of these parameters has been traditionally represented by the linear equations reproduced in Eqs. ((16) and (17)):

$$A(T) = A_2 - \frac{A_1}{RT} \quad (16)$$

$$B(T) = \frac{B_1}{RT} \quad (17)$$

where A_1 and B_1 are related to the intermolecular attractive and repulsive forces, respectively; while, A_2 is related to the non-ideal thermal pressure. However, it has been determined that for many fluids, A and B cannot be accurately represented by the first order relations. In such cases, higher-order temperature dependence of parameters has been considered; for instance, those which have been reproduced in Eqs. ((18) and (18)) [19]:

$$A(T) = A_1 + \frac{A_2}{T} + \frac{A_3}{T^2} \quad (18)$$

$$B(T) = B_1 + \frac{B_2}{T} + \frac{B_3}{T^2} \quad (19)$$

where A_i and B_i are fitting parameters to be determined from experimental data.

RESULTS AND DISCUSSION

In order to ascertain and perform a comparative study of the ability of the four lattice-hole theory based EOSs considered here, a comprehensive database comprised of 5740 experimental liquid density datapoints for 36 pure refrigerants, as listed in Table 1, was gathered. This table lists the pressure and temperature ranges for each substance alongside its respective references. The choice of the data sources was based on the inclusion of a high-pressure liquid region and a wide temperature range of liquid density data; in order to ensure that the obtained characteristic parameters of the pure components are representative over these expanded regions.

Table 1. Data Sources Used for Evaluating the Pure Component Characteristic Parameters of the EOSs. In This Table the Pressure and Temperature Values Have Been Rounded to the Closest Integer

Substance	Fitting range			
	P (MPa)	T (K)	N.D.	Ref.
CFCs				
Trichlorofluoromethane (R11)	1-20	273-468	159	[21]
Dichlorofluoromethane (R12)	0-61	150-524	182	[22–24]
1,1,2-Trichloro-1,2,2-trifluoroethane (R113)	0-24	253-486	154	[25]
1,2-Dichloro-1,1,2,2-tetrafluoroethane (R114)	1-10	310-400	143	[26]
Chloropentafluoroethane (R115)	4-60	174-350	252	[27]
HCFCs				
Dichlorodifluoromethane (R21)	5-15	273-473	122	[28]
Chlorodifluoromethane (R22)	1-500	120-523	204	[29–31]
2,2-Dichloro-1,1,1-trifluoroethane (R123)	1-35	176-457	132	[32,33]
1,2-Dichloro-1,2,2-trifluoroethane (R123a)	0-6	277-367	77	[34]
1-Chloro-1,2,2,2-tetrafluoroethane (R124)	1-36	104-400	149	[32]
1,1-Dichloro-1-fluoroethane (R141b)	1-69	180-400	61	[35,36]
1-Chloro-1,1-difluoroethane (R142b)	0-60	143-408	257	[27]
PFCs				
Tetrafluoromethane (R14)	0-57	94-224	86	[37]
Hexafluoroethane (R116)	10-50	173-288	105	[27]
Octafluoropropane (R218)	1-41	204-353	92	[38]
Perfluorocyclobutane (RC318)	0-174	233-473	150	[39,40]
HFCs				
Trifluoromethane (R23)	0-120	118-294	267	[27]
Fluoromethane (R41)	7-70	130-315	220	[27]
1,1,2,2-Tetrafluoroethane (R134)	0-5	200-367	69	[34,36]
1,1,1,2-Tetrafluoroethane (R134a)	5-60	293-373	107	[41]
1,1,1-Trifluoroethane (R143a)	3-35	166-344	108	[42]
1,1-Difluoroethane (R152a)	2-35	158-384	126	[42]
1,1,1,2,3,3,3-Heptafluoropropane (R227ea)	1-30	208-373	151	[43,44]
1,1,1,2,3,3-Hexafluoropropane (R236ea)	0-7	243-412	409	[45]
1,1,1,3,3,3-Hexafluoropropane (R236fa)	1-70	293-373	111	[46]
1,1,2,2,3-Pentafluoropropane (R245ca)	6-60	200-445	260	[34]
1,1,1,2,2-Pentafluoropropane (R245cb)	1-6	244-371	209	[34]
1,1,1,3,3-Pentafluoropropane (R245fa)	1-70	294-373	114	[46]
1,1,1,2,3,4,4,4-Octafluorobutane (R338eea)	0-6	242-372	397	[47]
1,1,1,3,3-Pentafluorobutane (R365mfc)	0-25	283-343	208	[48]

Table 1. Continued

HFES				
Pentafluorodimethyl ether (RE125)	5-35	243-326	161	[27]
Bis(difluoromethyl)ether (RE134)	1-5	274-367	63	[49]
Methyl trifluoromethyl ether (R143m)	0-7	240-370	255	[50]
Perfluoropropyl methyl ether (R347mcc)	0-4	250-437	115	[51,52]
Krytox® (Perfluoropolyether)	1-274	298-533	87	[53]
Methyl pentafluoroethyl ether (R245mc)	0-3	260-370	64	[51]
		Total:	5740	

Table 2. The AARD% of the Correlated Densities for the Pure Refrigerants Studied

Substance	AARD%			
	ϵ^* -Modified SL	Simha-Somcynsky	MSS-II	Park-Kim
CFCs				
Trichlorofluoromethane (R11)	1.276	0.885	1.725	0.912
Dichlorofluoromethane (R12)	2.293	2.305	2.989	2.059
1,1,2-Trichloro-1,2,2-trifluoroethane (R113)	1.038	1.203	0.647	0.817
1,2-Dichloro-1,1,2,2-tetrafluoroethane (R114)	0.218	0.586	0.832	0.171
Chloropentafluoroethane (R115)	0.453	0.482	0.425	0.480
Average for CFCs:	1.056	1.092	1.324	0.888
HCFCs				
Dichlorodifluoromethane (R21)	0.955	1.883	2.017	3.027
Chlorodifluoromethane (R22)	0.495	0.404	0.533	1.462
2,2-Dichloro-1,1,1-trifluoroethane (R123)	1.538	1.662	2.492	1.789
1,2-Dichloro-1,2,2-trifluoroethane (R123a)	0.029	0.029	0.370	0.119
1-Chloro-1,2,2,2-tetrafluoroethane (R124)	0.512	0.507	0.711	0.845
1,1-Dichloro-1-fluoroethane (R141b)	0.291	0.163	0.267	0.584
1-Chloro-1,1-difluoroethane (R142b)	0.879	0.617	0.591	0.794
Average for HCFCs:	0.671	0.752	0.997	1.231
PFCs				
Tetrafluoromethane (R14)	0.426	0.833	0.540	1.336
Hexafluoroethane (R116)	0.536	0.307	0.193	0.221
Octafluoropropane (R218)	0.295	0.657	0.378	0.362
Perfluorocyclobutane (RC318)	0.880	1.650	2.046	1.121
Average for PFCs:	0.534	0.861	0.789	0.760

Table 2. Continued

HFCs				
Trifluoromethane (R23)	0.516	0.234	0.274	0.790
Fluoromethane (R41)	0.448	0.393	1.328	1.539
1,1,2,2-Tetrafluoroethane (R134)	0.501	0.089	0.312	0.137
1,1,1,2-Tetrafluoroethane (R134a)	0.608	1.639	0.534	1.677
1,1,1-Trifluoroethane (R143a)	0.428	0.468	0.579	1.627
1,1-Difluoroethane (R152a)	0.989	0.511	0.659	0.518
1,1,1,2,3,3,3-Heptafluoropropane (R227ea)	0.595	0.768	0.758	0.810
1,1,1,2,3,3-Hexafluoropropane (R236ea)	0.427	0.442	0.324	1.955
1,1,1,3,3,3-Hexafluoropropane (R236fa)	0.215	0.419	0.423	2.763
1,1,2,2,3-Pentafluoropropane (R245ca)	0.849	0.502	0.534	0.405
1,1,1,2,2-Pentafluoropropane (R245cb)	1.086	0.913	1.118	0.249
1,1,1,3,3-Pentafluoropropane (R245fa)	0.229	0.258	0.244	0.153
1,1,1,2,3,4,4,4-Octafluorobutane (R338eea)	0.164	0.281	0.171	0.334
1,1,1,3,3-Pentafluorobutane (R365mfc)	0.140	0.153	0.064	0.048
Average for HFCs:	0.514	0.505	0.523	0.929
HFES				
Pentafluorodimethyl ether (RE125)	0.255	0.211	0.331	0.187
Bis(difluoromethyl)ether (RE134)	0.299	0.180	0.157	0.034
Methyl trifluoromethyl ether (R143m)	1.244	1.247	1.146	0.405
Perfluoropropyl methyl ether (R347mcc)	1.350	1.212	2.423	0.635
Krytox® (Perfluoropolyether)	0.884	0.463	0.496	0.504
Methyl pentafluoroethyl ether (R245mc)	0.213	0.069	0.103	0.070
Average for HFES:	0.708	0.564	0.776	0.306
Overall Average	0.654	0.684	0.798	0.859

CFCs: Chlorofluorocarbons; HCFCs: Hydrochlorofluorocarbons; PFCs: Perfluorocarbons; HFCS: Hydrofluorocarbons; HFES: Hydrofluoroethers

Furthermore, it should be noted that practical use of these lattice-hole theory based equations of state, aside from the ϵ^* -Modified Sanchez Lacombe EOS, involves simultaneous solving of the pertinent coupled equations by making use of an appropriate numerical method. In doing so, and by having the characteristic parameters of the EOS for each refrigerant, the only remaining unknown variables would become reduced volume (\tilde{V}) and occupied site fraction (y) for known values of temperature and pressure.

In other words, one can easily employ one of the readily available commercial or open-source numerical software solutions to simultaneously solve the coupled equations and obtain the molar volume and subsequently the liquid density. As for the choice of suitable initial points in the use of the numerical non-linear equation system solvers, and simply because the occupied site fraction, as its name suggests, takes values between zero and one, and also the reduced volume has values near 1, no major challenge

would be posed to the prospective use of these lattice-hole theory based equations of state.

Subsequently, the characteristic parameters of the four equations of state for each pure component were determined by minimizing the average absolute relative deviations (AARDs [%]) between calculated and experimental density data according to the objective function given in Eq. (19):

$$AARD(\%) = \frac{100}{ND} \sum_{i=1}^{ND} \left| \frac{\rho^{Calc.} - \rho^{Exp.}}{\rho^{Exp.}} \right| \quad (20)$$

The optimization procedure involved the consecutive use of a global followed by a local optimization algorithm. The evaluated characteristic parameters, alongside their respective units, are reported in the supplementary materials accompanying the online version of the article. Furthermore, to assess their relative performance, Table 2 reports the calculated AARD% deviations of the four equations of state in correlating the experimental liquid density data reported in Table 1.

As can be seen from the results obtained, no invariable

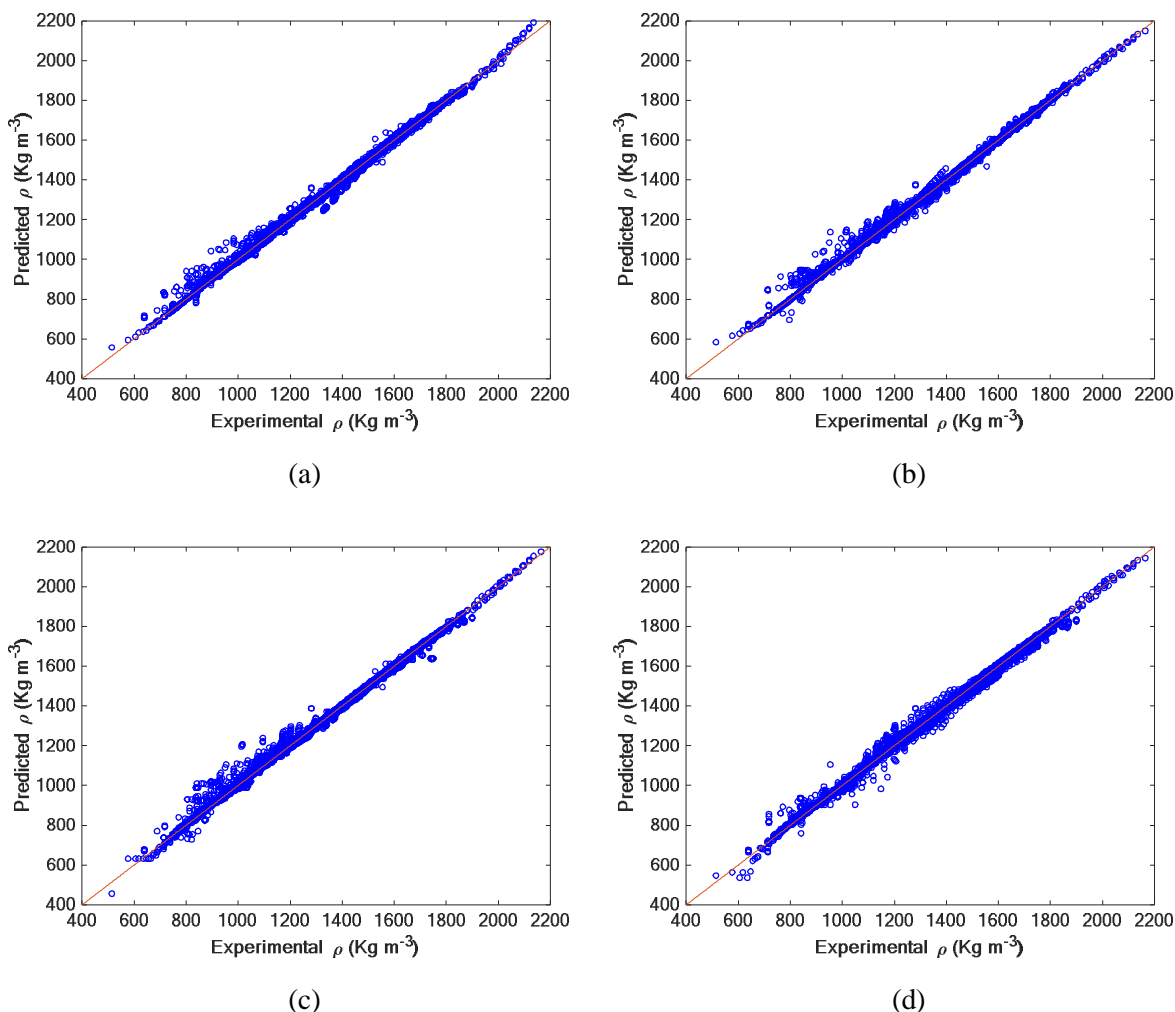


Fig. 1. Correlated vs. experimental liquid density for all the datapoints considered in the present study. (a): ϵ^* -Modified Sanchez-Lacombe EOS; (b): Simha-Somcynsky EOS; (c): MSS-II EOS; (d): Park-Kim EOS.

conclusion can be made about the superiority of any of the equations of state studied when it comes to representing the liquid density of refrigerants. Still and based on the average values, as for CFC and HFE refrigerants, Park-Kim EOS, as for HCFCs and PFCs, ϵ^* -Modified SL EOS and as for HFCs, Simha-Somcynsky EOS exhibit the highest accuracy. Nonetheless and on average, the ϵ^* -Modified Sanchez-Lacombe EOS demonstrates moderately higher accuracy when considering all the 36 refrigerants, with an average *AARD%* value of only 0.654%. Furthermore, the correlated values vs. the experimental liquid density data for all 36 refrigerants studied are plotted in Fig. 1; revealing the

generally good agreement between the correlated values from lattice-hole theory based equations of state and the experimental datapoints.

Furthermore, in order to ascertain how the performance of the equations of state are affected by temperature, Fig. 2 presents a graphical representation of the average absolute relative deviations of all the isotherms studied as a function of the reduced temperature. The same trend, that is observable for all the four equations of state studied, is the decrease in correlation accuracy as the temperature approaches its critical value. Although this fact certainly leaves room for further improvements, the amount of

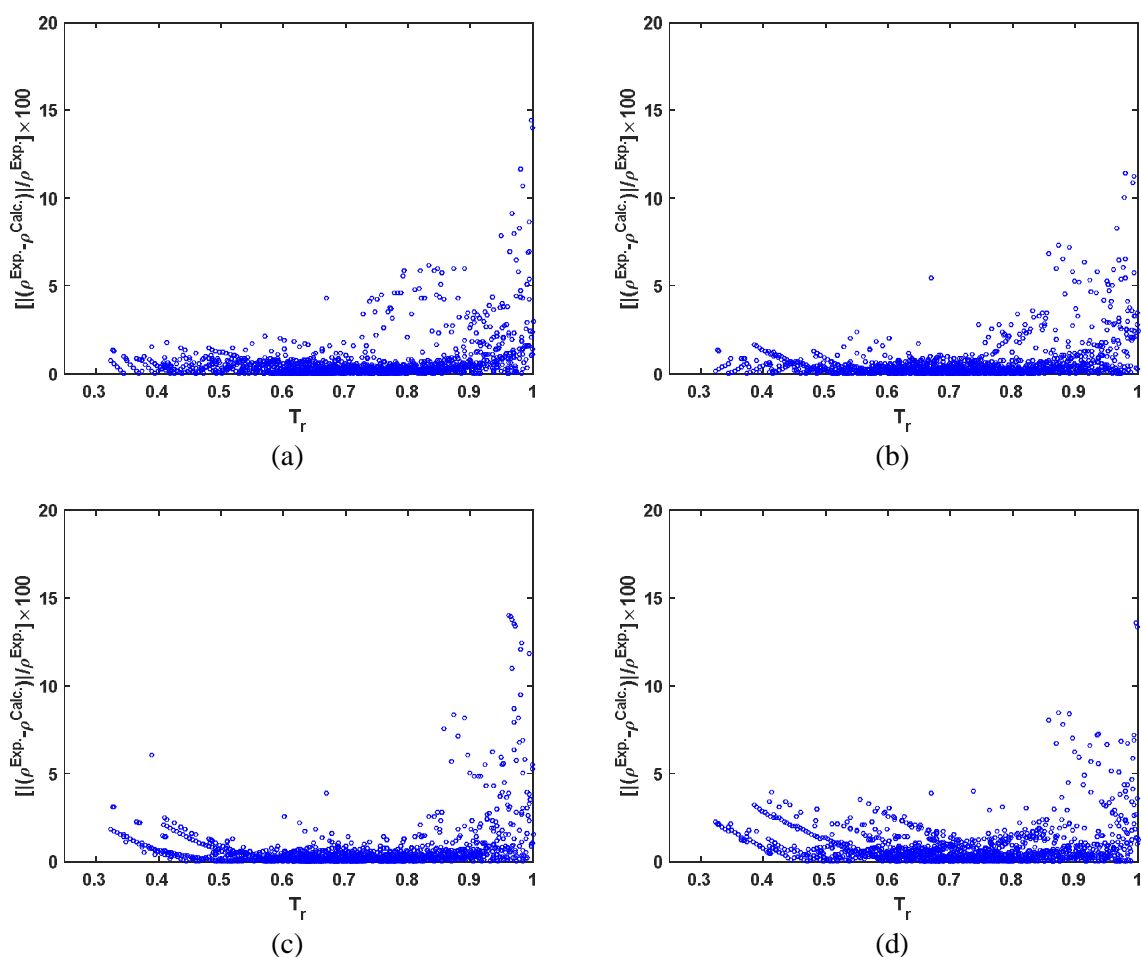


Fig. 2. The *AARD%* of all the isotherms for 35 of the refrigerants considered in the present study as a function of T_r . (a): ϵ^* -Modified Sanchez-Lacombe EOS; (b): Simha-Somcynsky EOS; (c): MSS-II EOS; (d): Park-Kim EOS.

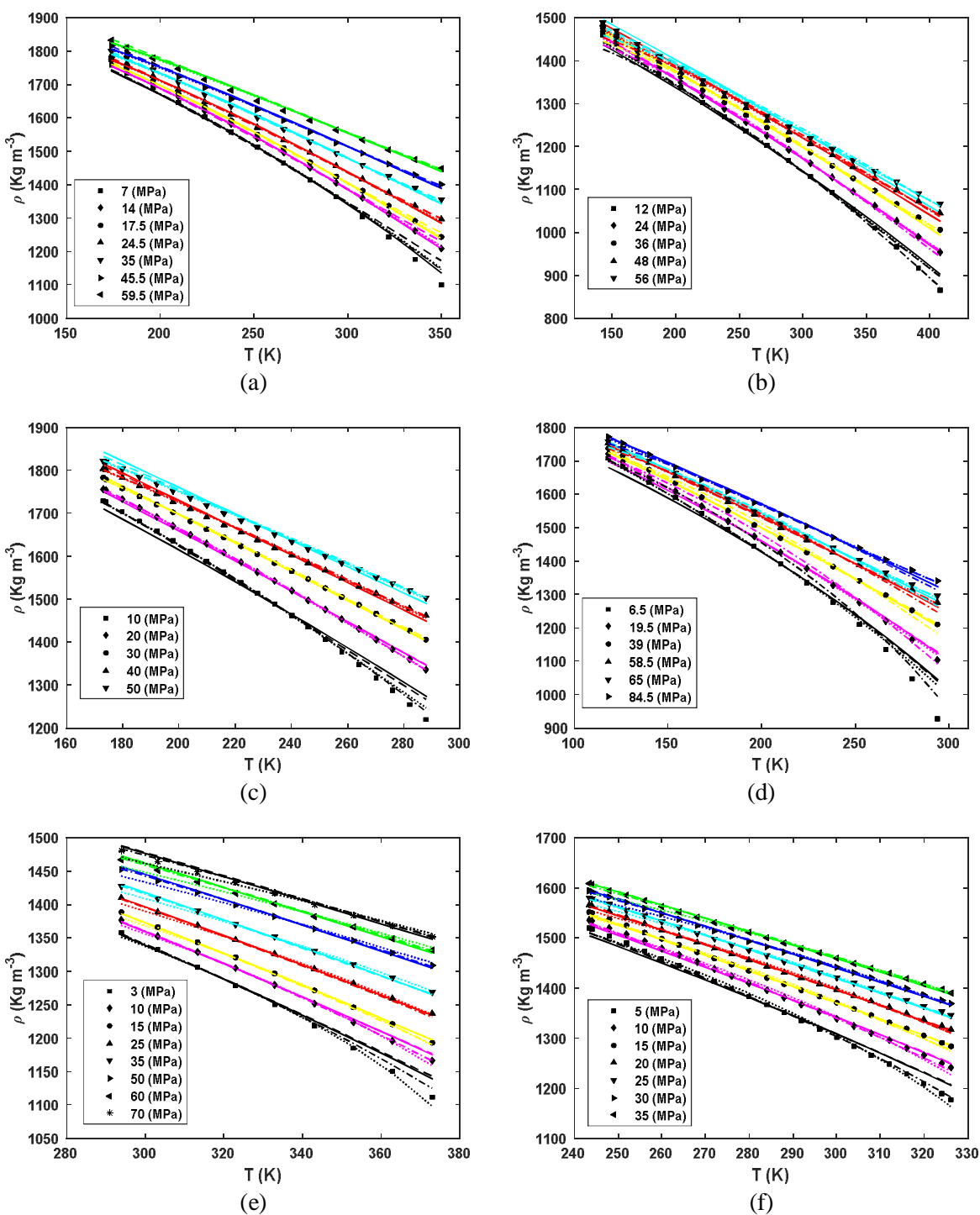


Fig. 3. Graphical representation of the liquid density of pure refrigerants vs. temperature. (a): Chloropentafluoroethane (R115); (b): 1-Chloro-1,1-difluoroethane (R142b); (c): Hexafluoroethane (R116); (d): Trifluoromethane (R23); (e): 1,1,1,3,3-Pentafluoropropane (R245fa); (f): Pentafluorodimethyl ether (RE125). (Legend: — ϵ^* -Modified Sanchez-Lacombe EOS; - - - - Simha-Somcynsky EOS; MSS-II EOS; - . - . - . Park-Kim EOS; also, symbols denote experimental data.)

inaccuracies introduced in the high temperature range is generally not to the extent that make the use of the studied equations of state in these conditions inadvisable, except for very precise calculations. In constructing these plots, the values of the refrigerants critical temperatures have been retrieved mainly from “NIST/TRC Web Thermo Tables (WTT)” alongside other literature sources [27,49,54-56]. Still, as the critical temperature of Krytox® is not available in the open literature as of yet, this refrigerant has been excluded from Fig. 2. Quantitatively and by considering

only the datapoints with $T_r > 0.8$, average absolute relative deviations of 1.124%, 1.212%, 1.556%, 1.255% are obtained for ϵ^* -Modified Sanchez-Lacombe, Simha-Somcynsky, MSS-II and Park-Kim EOSs, respectively.

Additionally, Fig. 3 illustrates the plot of the liquid density as a function of temperature and pressure for a representative component from each of the five refrigerant types studied. Note that in order to prevent the plots from becoming excessively cluttered; only a subset of the isobars have been plotted for each pure refrigerant.

Table 3. The AARD% of the Predicted Densities from Peng-Robinson (PR) and Linear Isotherm Regularity (LIR) EOSs Alongside the Critical Constants and Acentric Factors of the Pure Refrigerants Studied

Substance	T_c (K)	P_c (MPa)	ω	AARD%	
				PR	LIR
CFC					
Trichlorofluoromethane (R11)	471.110	4.408	0.188	5.942	1.147
Dichlorofluoromethane (R12)	385.120	4.136	0.176	13.100	5.931
1,1,2-Trichloro-1,2,2-trifluoroethane (R113)	487.210	3.392	0.255	5.200	1.491
1,2-Dichloro-1,1,2,2-tetrafluoroethane (R114)	420.608	3.352	0.246	7.117	0.130
Chloropentafluoroethane (R115)	353.100	3.129	0.249	8.459	0.776
Average for CFCs:				7.964	1.895
HCFCs					
Dichlorodifluoromethane (R21)	452.720	5.289	0.202	5.129	3.281
Chlorodifluoromethane (R22)	369.295	4.990	0.215	158.876	6.240
2,2-Dichloro-1,1,1-trifluoroethane (R123)	456.830	3.662	0.283	3.164	8.808
1,2-Dichloro-1,2,2-trifluoroethane (R123a)	461.600	3.750	0.303	4.602	0.236
1-Chloro-1,2,2,2-tetrafluoroethane (R124)	395.428	3.625	0.300	2.920	2.296
1,1-Dichloro-1-fluoroethane (R141b)	477.500	4.212	0.217	3.328	3.024
1-Chloro-1,1-difluoroethane (R142b)	410.260	4.050	0.232	2.574	2.549
Average for HCFCs:				25.799	3.776
PFC					
Tetrafluoromethane (R14)	227.396	3.762	0.176	10.128	3.839
Hexafluoroethane (R116)	293.030	3.048	0.255	9.229	0.254
Octafluoropropane (R218)	345.020	2.640	0.326	8.002	3.083
Perfluorocyclobutane (RC318)	388.370	2.778	0.351	8.024	1.144
Average for PFCs:				8.846	2.080

Table 3. Continued

HFCs					
Trifluoromethane (R23)	299.293	4.832	0.253	4.007	1.137
Fluoromethane (R41)	317.280	5.906	0.177	11.154	1.134
1,1,2,2-Tetrafluoroethane (R134)	391.752	4.607	0.293	2.595	2.896
1,1,1,2-Tetrafluoroethane (R134a)	374.210	4.059	0.326	1.363	0.141
1,1,1-Trifluoroethane (R143a)	345.857	3.762	0.262	4.653	2.606
1,1-Difluoroethane (R152a)	386.410	4.517	0.259	7.034	2.224
1,1,1,2,3,3,3-Heptafluoropropane (R227ea)	374.900	2.925	0.358	4.659	2.384
1,1,1,2,3,3-Hexafluoropropane (R236ea)	419.014	3.786	0.370	13.405	5.390
1,1,1,3,3,3 Hexafluoropropane (R236fa)	398.070	3.200	0.375	4.348	0.233
1,1,2,2,3-Pentafluoropropane (R245ca)	444.746	3.739	0.358	1.330	1.083
1,1,1,2,2-Pentafluoropropane (R245cb)	380.090	3.136	0.302	2.780	1.020
1,1,1,3,3-Pentafluoropropane (R245fa)	427.160	3.651	0.378	3.884	0.151
1,1,1,2,3,4,4,4-Octafluorobutane (R338eea)	421.650	-	-	-	1.615
1,1,1,3,3-Pentafluorobutane (R365mfc)	460.000	3.266	0.371	4.906	0.141
Average for HFCs:				5.086	1.582
HFEs					
Pentafluorodimethyl ether (RE125)	354.490	3.355	0.336	4.147	0.116
Bis(difluoromethyl)ether (RE134)	420.250	4.228	0.353	1.642	1.092
Methyl trifluoromethyl ether (R143m)	377.920	3.640	0.238	7.463	0.921
Perfluoropropyl methyl ether (R347mcc)	437.650	2.480	0.424	3.105	3.534
Krytox® (Perfluoropolyether)	-	-	-	-	0.607
Methyl pentafluoroethyl ether (R245mc)	406.820	2.887	0.354	3.906	1.139
Average for HFEs:				4.053	1.235
Overall Average				10.064	2.050

Figures 2 and 3 reveal that the midrange temperatures and pressures, relative to each component's critical constants, are the conditions over which the four lattice-hole theory based equations of state studied can most accurately correlate the liquid density of refrigerants. Nonetheless, their overall performance is satisfactory even in the extreme conditions for most general purposes.

Moreover, to ascertain how these lattice-hole theory based equations of state, which formulation has sound justification rooted in statistical thermodynamics, perform relative to other equations of state, and determine whether their augmented accuracy warrants the added complexity inherent in using them, Table 3 presents the *AARDs* of the commonly used Peng-Robinson EOS as well as the linear

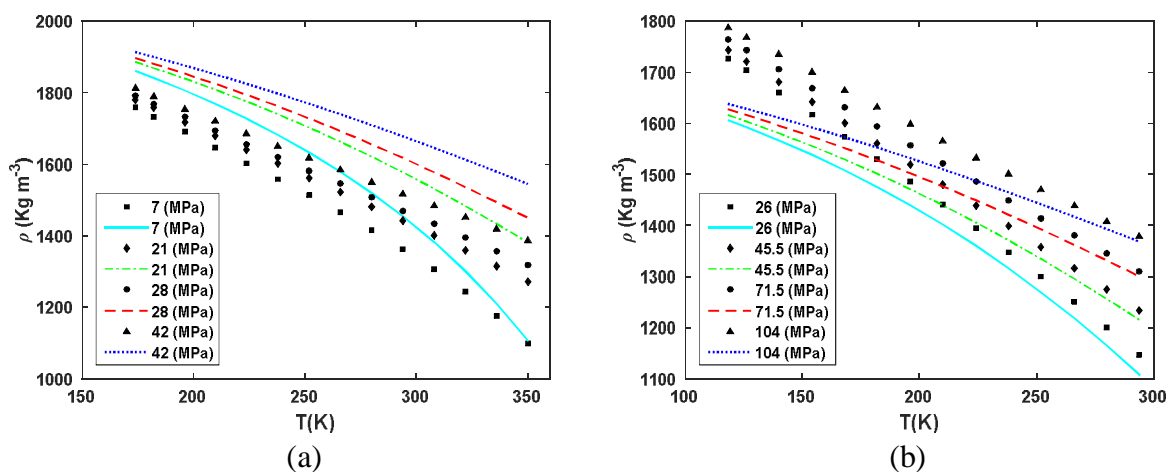


Fig. 4. Liquid density of pure refrigerants vs. temperature obtained using Peng-Robinson EOS. (a): Chloropentafluoroethane (R115); (b): Trifluoromethane (R23). Symbols denote experimental data and lines represent the Peng-Robinson EOS.

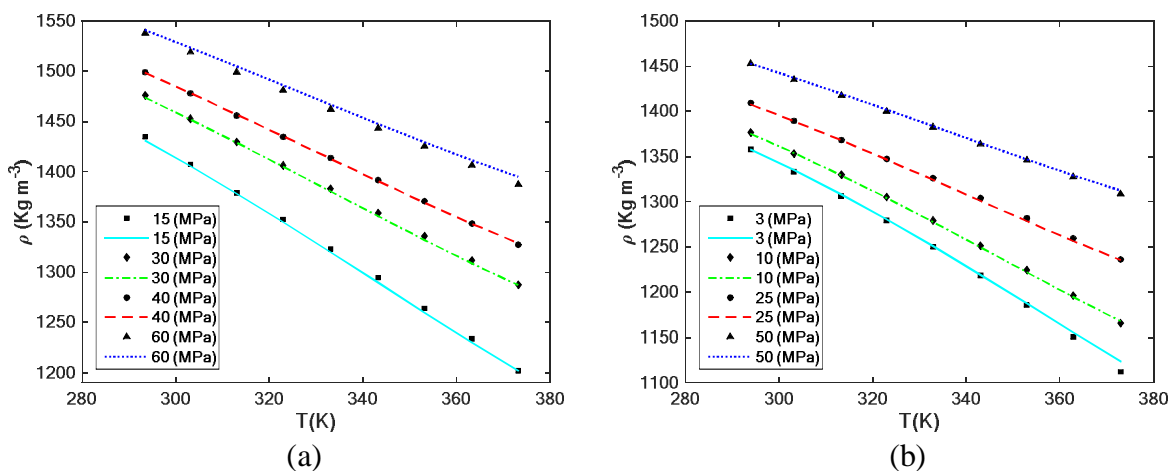


Fig. 5. Liquid density of pure refrigerants vs. temperature obtained using linear isotherm regularity EOS. (a): 1,1,1,3,3,3 Hexafluoropropane (R236fa); (b): 1,1,1,3,3-Pentafluoropropane (R245fa). Symbols denote experimental data and lines represent the linear isotherm regularity EOS.

isotherm regularity EOS in correlating the experimental liquid density data reported in Table 1. Also included in this table are the available critical constants as well as the acentric factors of the pure refrigerants studied [27,57]. In regards to the linear isotherm regularity EOS, it should be noted that after investigating several different correlations, it was determined that the temperature dependence of the A and B parameters of the EOS (Eq. (14)), could be well represented by a quadratic polynomial of temperature; the coefficients of which were determined and reported in the supplementary materials accompanying the online version of the article. As can be seen from Table 3, the lattice-hole theory based EOSs almost always demonstrate higher accuracy. This trend can be particularly seen in the very high pressure and temperature ranges; especially, in the case of Chlorodifluoromethane (R22) Peng-Robinson EOS exhibits considerable deviations in the highly compressed region. Moreover, a graphical representation of the liquid density for a few isobars of four representative refrigerants, obtained using the Peng-Robinson as well as the linear isotherm regularity EOSs is presented in Figs. 4 and 5. A quick comparison between these figures and also Table 3 with those obtained using the four lattice-hole theory based EOSs studied, *i.e.* Fig. 3 and Table 2, reveals the generally higher accuracy of the lattice-hole theory based EOSs in modeling the volumetric properties of pure refrigerants.

CONCLUSIONS

In the present study the performance of four equations of state that are based on lattice-hole theory are for the first time investigated in correlating the liquid density of pure refrigerants. In doing so, a sizable database comprised of the experimental liquid density data of 36 refrigerants belonging to five different types and covering a wide temperature and pressure ranges was gathered. Employing both global and local optimization algorithms, the pure component characteristic parameters of the four equations of state were determined and used in their comparative study. According to the results obtained, all the four EOSs are quite satisfactory in representing the liquid density of refrigerants. Nonetheless and on average, the ϵ^* -Modified Sanchez-Lacombe EOS demonstrates a slightly more precise performance. As for their performance near

the critical temperature of the pure refrigerants, which is considered as a suitable benchmark for testing different equations of state, the ϵ^* -Modified Sanchez-Lacombe EOS once again exhibits a moderately superior performance, closely followed by Simha-Somcynsky, Park-Kim and MSS-II equations of state. Additionally, a comparison is made with the commonly used Peng-Robinson as well as the linear isotherm regularity EOSs, that demonstrates the large improvements obtained when using the lattice-hole theory based EOSs do justify the use of these more complex equations of state for modeling the volumetric properties of various pure refrigerants.

APPENDIX A. SUPPLEMENTARY MATERIALS

Supplementary data associated with this article that tabulate the pure refrigerant characteristic parameters of the EOSs could be found accompanying the online version of it. Note that the spreadsheet provided has been categorized into five workbook sheets, each belonging to one EOS. Also keep in mind that all the estimated EOS parameters are reproduced in their original *IEEE* double-precision floating-point format, but rounding the numeric values to only 3 digits of precision will not introduce any major deviation and the results obtained would still be quite satisfactory.

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