# Equations of state for the thermodynamic properties of *n*-perfluorobutane, *n*-perfluoropentane, and *n*perfluorohexane

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# Abstract

Helmholtz energy equations of state with independent variables of temperature and density were developed for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane based on experimental thermodynamic property data from the literature and molecular simulation results (for *n*-perfluorobutane) of this work. The ranges of validity for temperature, pressure, and density of the equations of state for these three fluids were determined from the available data. The uncertainties in density, vapor pressure, saturated liquid and vapor densities, and caloric properties of the equations of state were also estimated from comparisons with the data. The behavior of thermodynamic properties was analyzed to assess the quality of the equations of state; they have reasonable behavior within the range of validity, as well as at high temperatures and pressures, and temperatures far below the triple point temperature.

KEYWORDS: *n*-perfluorobutane, *n*-perfluoropentane, *n*-perfluorohexane, equation of state, thermodynamic property, Helmholtz energy

#### **1.** Introduction

*n*-Perfluorobutane (C<sub>4</sub>F<sub>10</sub>, CAS no. 355-25-9), *n*-perfluoropentane (C<sub>5</sub>F<sub>12</sub>, CAS no. 678-26-2), and *n*-perfluorohexane (C<sub>6</sub>F<sub>14</sub>, CAS no. 355-42-0) are saturated fluorocarbons that are very stable because of the strength of the C-F bond.<sup>1</sup> Perfluorocarbons and other fluorocarbons have attracted attention in academia, industry, and medicine because of their remarkable physical and chemical properties.<sup>2</sup> In academia, the discovery of fluorocarbons added a new chemical family that is different from but along the same line as organic compounds.<sup>3</sup> In the 1950s, many researchers studied various theories between like and unlike molecules in binary mixtures. They found an anomalous behavior in fluorocarbon solutions that has large positive deviations from Raoult's law.<sup>4</sup> Scott reviewed both the experimental measurements (vapor pressures, solubilities, heats of mixing,

and volume changes) and publications that gave explanations for the anomalous behavior of fluorocarbon solutions in the 1950s.<sup>5</sup> In industry, fluorocarbons are used as refrigerants (because of their low boiling point and freezing point temperatures), fire extinguishing agents, dielectric media, solvents, and foam blowing agents.<sup>2, 6</sup> Because perfluorocarbons are immiscible with many common organic solvents, but have a high ability to dissolve gases,<sup>2</sup> it is worth investigating the absorption capabilities of perfluorocarbons in common petroleum refinery gases. In medicine,<sup>6</sup> perfluorocarbon liquids can be used as fluorocarbon blood substitutes to replace blood because of their high chemical stability and solubility to oxygen. Even though perfluorocarbons have many advantages, they are also greenhouse gases that contribute to climate change when they are discharged into the atmosphere.

The application of these three perfluorocarbons requires thermodynamic properties, which can be obtained from equations of state. The most common multi-parameter formulation is based on the Helmholtz energy with independent variables of temperature and density. It can comprehensively describe the thermodynamic properties of fluids with low uncertainties and wide application ranges, and without the need for integration, as with pressure explicit equation of state to obtain caloric properties.

Brown and Mears<sup>7</sup> and Brown<sup>8</sup> developed Martin-Hou equations of state for  $C_4F_{10}$  and  $C_6F_{14}$ , respectively. Extended corresponding states models have been developed for  $C_4F_{10}$  and  $C_5F_{12}$  by Huber and Ely.<sup>9</sup> However, they have high uncertainties in thermodynamic properties due to the extremely limited experimental data available when the models were developed. In this work, Helmholtz energy equations of state for these three perfluorocarbons were developed that are valid over all liquid, vapor, and critical region states, and which are based on the available thermodynamic property data from the literature and molecular simulation results for *n*-

perfluorobutane.

#### 2. **Triple, Normal-Boiling, and Critical Points**

Symbol	Property	<i>n</i> -Perfluorobutane	<i>n</i> -Perfluoropentane	<i>n</i> -Perfluorohexane	Unit
	CAS no.	355-25-9	678-26-2	355-42-0	
R	Molar gas constant		8.314462618		$J \cdot mol^{-1} \cdot K^{-1}$
М	Molar mass	238.027	288.034	338.042	g·mol <sup>−1</sup>
$T_{\rm c}$	Critical temperature	386.326	421.0	448.0	ĸ
$p_{ m c}$	Critical pressure	2322.4	2063.0	1741.6	kPa
$ ho_{ m c}$	Critical density	2.637	2.17	1.825	mol·dm <sup>-3</sup>
$T_{ m tp}$	Triple-point temperature <sup>10</sup>	144.0	148.21	187.07	K
$p_{ m tp}$	Triple-point pressure	0.0010766	0.00010638	0.0041329	kPa
$ ho_{ m tpv}$	Vapor density at the triple point	8.99×10 <sup>-7</sup>	8.63×10 <sup>-8</sup>	$2.66 \times 10^{-6}$	mol·dm <sup>-3</sup>
$ ho_{ m tpl}$	Liquid density at the triple point	8.604	7.118	5.881	$mol \cdot dm^{-3}$
$T_{ m nbp}$	Normal-boiling-point temperature	271.123	302.453	330.274	Κ
$ ho_{ m nbpv}$	Vapor density at the normal- boiling point	0.0472	0.0427	0.0394	$mol \cdot dm^{-3}$
$ ho_{ m nbpl}$	Liquid density at the normal- boiling point	6.705	5.522	4.669	$mol \cdot dm^{-3}$
ω	Acentric factor	0.372	0.436	0.497	
$T_0$	Reference temperature for ideal-gas properties	273.15	273.15	273.15	К
$p_0$	Reference pressure for ideal- gas properties	1.0	1.0	1.0	kPa
$h_0^0$	Reference ideal-gas enthalpy at $T_0$	23978.6621588168	19950.2774798140	13334.6172770744	$J \cdot mol^{-1}$
$s_{0}^{0}$	Reference ideal-gas entropy at $T_0$ and $p_0$	126.4487693542	102.7828432107	73.6733472083	$J \cdot mol^{-1} \cdot K^{-1}$
Т	Temperature range	144.0-450	148.21-500	187.07-450	Κ
$p_{\max}$	Maximum pressure	10	10	40	MPa
$ ho_{ m max}$	Maximum density	8.61	7.12	5.89	mol·dm <sup>−3</sup>

<sup>*a*</sup>All properties in this table were determined in this work except R, M, and  $T_{\rm tp}$ .

Table 1 displays the physical constants and characteristic properties of *n*-perfluorobutane, *n*perfluoropentane, and *n*-perfluorohexane, and gives the critical parameters used in the equations of state reported here. The critical parameters are important properties for fluids because they are used as reducing parameters; incorrect values for the critical point will increase the difficulty of obtaining the near zero slope of pressure with respect to density along the critical isotherm in the critical region. They are also needed for developing the ancillary equations for vapor pressure and saturation densities. Tables 2 to 4 show published triple-point, normal-boiling-point, and criticalpoint values of these three fluids, with temperatures converted to ITS-90 where necessary. The

triple-point temperatures are the recommended values from the Thermodynamic Data Engine (TDE) program<sup>10</sup> available from the Thermodynamic Research Center (TRC) of NIST. The critical pressure, normal-boiling-point temperatures, and saturated liquid and vapor densities were calculated from the respective equation of state. The critical temperatures and densities were determined while fitting the equations' behavior in the vicinity of the critical region. The triple-point, normal-boiling-point, and critical parameters of this work are given in Table 1. Figure 1 shows the behavior of temperature versus density near the critical region for the equation of state for *n*-perfluorobutane. From this figure, the rectilinear diameter (the average of the saturated liquid and vapor densities) of *n*-perfluorobutane has reasonable behavior and is nearly straight up to the critical-point.<sup>11-13</sup> The other two fluids show similar behavior in the value of the critical density. The value of the critical temperature falls within the range of published critical temperatures.



Figure 1. The behavior of the equation of state for *n*-perfluorobutane in the vicinity of the critical region.

Table 2.	Triple-	ooint,	normal-b	oiling-p	ooint,	and	critical-	point	values	of <i>n</i> -	perfluorob	ıtane

	Temperature T	Pressure p	Density $\rho$
Reference	K	MPa	mol·dm <sup>-3</sup>
	Triple Point		
Campos-Vallette et al. (1982) <sup>14</sup>	144.015		
This work	144.0		
	Normal Boiling Point		
Gilmour <i>et al.</i> (1967) <sup>15</sup>	271.002		6.711
Simons and Mausteller (1952) <sup>16</sup>	259.961		6.925
This work	271.123		6.705
	Critical Point		
Ahmar <i>et al.</i> $(2011)^2$	385.84	2.289	

Brown and Mears (1958) <sup>7</sup>	386.326	2.3234	2.521	
Fowler <i>et al.</i> $(1947)^{17}$	386.426	2.3305		
Köster <i>et al.</i> (2012) <sup>18</sup>	385.84	2.29		
Soo <i>et al.</i> $(2010)^{19}$	386.4	2.29		
Valtz and Coquelet (2012) <sup>20</sup>	386.33	2.323		
Valtz <i>et al.</i> (2011) <sup>21</sup>	385.84	2.289		
Varuschenko et al. (1987) <sup>22</sup>	386.372	2.323	2.646	
Zawisza (1967) <sup>23</sup>	385.811	2.2899	2.688	
This work	386.326	2.3224	2.637	

 Table 3. Triple-point, normal-boiling-point, and critical-point values of *n*-perfluoropentane

	Temperature T	Pressure p	Density $\rho$
Reference	K	MPa	mol·dm <sup>-3</sup>
	Triple Point		
Burger <i>et al.</i> (1951) <sup>24</sup>	147.812		
Crowder <i>et al.</i> (1967) <sup>25</sup>	148.363		
This work	148.21		
	Normal Boiling Point		
Barber and Cady (1956) <sup>26</sup>	302.483		
Burger <i>et al.</i> (1951) <sup>24</sup>	302.433		5.503
Crowder <i>et al.</i> (1967) <sup>25</sup>	302.193		
Narayana and Swamy (1989) <sup>27</sup>	302.153		
This work	302.453		5.522
	Critical Point		
Aftienjew and Zawisza (1977) <sup>28</sup>	420.555	2.045	2.116
Ermakov and Skripov (1967) <sup>29</sup>	421.835	2.04	2.610
Ermakov and Skripov (1969) <sup>30</sup>			2.149
Vandana <i>et al.</i> $(1994)^{31}$	420.9		2.159
Varuschenko et al. (1987) <sup>22</sup>	421.965	2.037	2.188
This work	421.0	2.063	2.17

#### Table 4. Triple-point, normal-boiling-point, and critical-point values of *n*-perfluorohexane

	Temperature T	Pressure p	Density $\rho$						
Reference	K	MPa	mol·dm <sup>-3</sup>						
	Triple Point								
Campos-vallette et al. (1982) <sup>14</sup>	185.012								
Crowder et al. (1967) <sup>25</sup>	187.493								
Dunlap <i>et al.</i> (1958) <sup>32</sup>	186.933								
Starkweather (1986) <sup>33</sup>	182.426								
Stiles and Cady (1952) <sup>34</sup>	187.143								
This work	187.07								
Normal Boiling Point									
Cheng and McCoubrey (1963) <sup>35</sup>	329.725								
Narayana and Swamy (1989) <sup>27</sup>	330.145								
This work	330.274								
	Critical Point								
Cheng and McCoubrey (1963) <sup>35</sup>	449.544								
Dunlap <i>et al.</i> (1958) <sup>32</sup>	447.643								
Ermakov and Skripov (1967) <sup>29</sup>	451.645	1.91	2.258						
Ermakov and Skripov (1969) <sup>30</sup>			1.807						
Mousa (1978) <sup>36</sup>	448.764	1.8681	1.650						
Mousa <i>et al</i> . (1972) <sup>37</sup>	448.732	1.8681	1.651						
Skripov et al. (1977) <sup>38</sup>	449.106	1.905							
Taylor <i>et al</i> . (1970) <sup>39</sup>	450.962	1.8340	1.802						
Vandana <i>et al.</i> (1994) <sup>31</sup>	451.1	1.859							
Vandana <i>et al.</i> (1994) <sup>31</sup>	451.7		1.837						
This work	448.0	1.7416	1.825						

# **3.** Ancillary Equations

Ancillary equations including the vapor pressure, the saturated liquid density, and the saturated vapor density equations provide initial estimates for use in iterative Maxwell equilibrium calculations of saturation properties. Therefore, they are developed to expedite the iterative calculations during the fitting process of equations of state. The critical parameters used in the following relations are given in Table 1. The coefficients of the ancillary equations for n-perfluorobutane, n-perfluoropentane, and n-perfluorohexane are listed in Table 5.

Table 5. Coefficients of the ancillary equations for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane

Cultater a		Vapor Pre	essure	Saturated Liq	uid Density	Saturated Vapo	or Density
Substance	1 -	ni	ti	ni	ti	ni	ti
	1	-8.2957	1.0	7.2166	0.507	-6.2029	0.496
	2	4.5997	1.5	-18.074	0.824	7.0601	0.82
	3	-4.4355	1.9	32.084	1.15	-11.424	1.17
<i>n</i> -Periluorodutane	4	-5.0941	4.3	-30.238	1.5	-24.160	3.3
	5	-4.1863	15.1	12.446	1.9	-67.136	6.8
	6					-182.16	15.0
	1	-8.4733	1.0	3.9956	0.464	-4.456	0.479
	2	3.5899	1.5	-4.6464	0.9	-7.6886	1.51
n-Perfluoropentane	3	-3.3162	1.97	8.1411	1.4	-24.64	3.35
	4	-4.1966	3.63	-7.7694	1.9	-62.48	6.71
	5	-1.6897	11.74	3.4916	2.6	-163.57	14.76
	1	-9.0231	1.0	4.5417	0.463	-4.9298	0.476
	2	5.1365	1.5	-5.3549	0.85	-13.949	1.88
n-Perfluorohexane	3	-4.8413	1.9	5.7116	1.25	-53.702	4.73
	4	-5.2906	3.75	-2.6333	1.75	-113.62	10.4
	5	-2.937	11.7	1.1928	3.45	-262.16	21.05

#### **3.1.** Vapor pressure equations

The vapor pressure equation is

$$\ln\left(\frac{p_{\sigma}}{p_{c}}\right) = \frac{T_{c}}{T} \sum_{i} n_{i} \theta^{t_{i}} , \qquad (1)$$

where  $\theta = (1 - T/T_c)$ , *T* is the temperature,  $T_c$  is the critical temperature,  $p_\sigma$  is the vapor pressure,  $p_c$  is the critical pressure, and the coefficients  $n_i$  and exponents  $t_i$  of  $\theta$  were obtained through fitting. For *n*-perfluorobutane, the maximum deviation is 0.022 % between calculated values from this equation and values obtained from the full solution of the saturation properties with the use of the Maxwell criterion at temperatures from the triple-point temperature (144.0 K) to the critical temperature (386.326 K). For *n*-perfluoropentane, the maximum deviation is 0.028 % at temperatures from the triple-point temperature (148.21 K) to the critical temperature (421.0 K). For *n*-perfluorohexane, the maximum deviation is 0.068 % at temperatures from the triple-point temperature (187.07 K) to the critical temperature (448.0 K).

#### **3.2.** Saturated liquid density equations

The saturated liquid density equation can be represented as

$$\frac{\rho'}{\rho_{\rm c}} = 1 + \sum_{i} n_i \theta^{t_i} , \qquad (2)$$

where  $\rho'$  is the saturated liquid density and  $\rho_c$  is the critical density. For *n*-perfluorobutane, the maximum deviation is 0.046 % between calculated values from this equation and values obtained from the full solution of the saturation properties with the use of the Maxwell criterion at temperatures below 340 K and a maximum of 0.097 % at higher temperatures. For *n*-perfluoropentane, the maximum deviation is 0.017 % at temperatures below 365 K and a maximum of 0.061 % at higher temperatures. For *n*-perfluorohexane, the maximum deviation is 0.029 % at temperatures below 380 K and a maximum of 0.098 % at higher temperatures.

#### 3.3. Saturated vapor density equations

The saturated vapor density equation is

$$\ln\left(\frac{\rho''}{\rho_{\rm c}}\right) = \sum_{i} n_i \theta^{t_i} , \qquad (3)$$

where  $\rho$ " is the saturated vapor density. For *n*-perfluorobutane, the maximum deviation is 0.036 % between calculated values from this equation and values obtained from the full solution of the saturation properties with the use of the Maxwell criterion at temperatures below 345 K and a maximum of 0.14 % at higher temperatures. For *n*-perfluoropentane, the maximum deviation is 0.027 % at temperatures below 400 K and a maximum of 0.061 % at higher temperatures. For *n*-

perfluorohexane, the maximum deviation is 0.04 % at temperatures below 380 K and a maximum of 0.16 % at higher temperatures.

# 4. Helmholtz Energy Equations of State

The equations of state developed in this work are explicit in the Helmholtz energy with independent variables of temperature and density, and are given by

$$a(T,\rho) = a^0(T,\rho) + a^r(T,\rho), \qquad (4)$$

where *a* is the molar Helmholtz energy,  $a^0$  is the ideal-gas molar Helmholtz energy, and  $a^r$  is the residual molar Helmholtz energy, which corresponds to the influence of intermolecular forces.<sup>40</sup>

Its dimensionless reduced formulation is

$$\alpha(\tau,\delta) = \frac{a(T,\rho)}{RT} = \frac{a^0(T,\rho)}{RT} + \frac{a^r(T,\rho)}{RT} = \alpha^0(\tau,\delta) + \alpha^r(\tau,\delta),$$
(5)

where  $\alpha$  is the dimensionless reduced Helmholtz energy, *R* is the molar gas constant given in Table 1,  $\tau$  is the reciprocal reduced temperature  $\tau = T_c/T$ , and  $\delta$  is the reduced density  $\delta = \rho/\rho_c$ .  $T_c$  and  $\rho_c$  are the critical temperature and density given in Table 1.

#### 4.1. Properties of the ideal gas

The dimensionless ideal-gas Helmholtz energy can be calculated from the following formula,

$$\alpha^{0}(\tau,\delta) = \frac{a^{0}(\tau,\delta)}{RT} = \frac{h_{0}^{0}\tau}{RT_{c}} - \frac{s_{0}^{0}}{R} - 1 + \ln\frac{\delta\tau_{0}}{\delta_{0}\tau} - \frac{\tau}{R}\int_{\tau_{0}}^{\tau}\frac{c_{p}^{0}}{\tau^{2}}d\tau + \frac{1}{R}\int_{\tau_{0}}^{\tau}\frac{c_{p}^{0}}{\tau^{2}}d\tau, \qquad (6)$$

where  $c_p^0$  is the ideal-gas isobaric heat capacity,  $\tau_0 = T_c/T_0$ ,  $\delta_0 = \rho_0/\rho_c$ , and  $\rho_0$  is the ideal-gas density at the reference state, which can be calculated from the ideal-gas equation of state. In this work, we use  $T_0 = 273.15$  K and  $p_0 = 1.0$  kPa, thus  $\rho_0 = p_0/RT_0$ . The quantities  $h_0^0$  and  $s_0^0$  are arbitrary constants used to set the enthalpy and entropy to a prescribed reference state.

In Equation 6, the ideal-gas properties require the ideal-gas isobaric heat capacity equation. Its

common form is

$$\frac{c_p^0}{R} = c_0 + \sum_{k=1}^n v_k \left(\frac{u_k}{T}\right)^2 \frac{\exp(u_k/T)}{\left[\exp(u_k/T) - 1\right]^2},$$
(7)

where *n* is the number of Einstein-Planck terms, and  $v_k$  and  $u_k$  are the parameters of the Einstein terms that were determined while fitting the equation of state, which are given in Table 6. Idealgas isobaric heat capacity from the TDE program<sup>10</sup> are the only data available, which were calculated based on the method of Wilhoit.<sup>41</sup> Their average absolute relative deviations are shown in Table 7. Figure 2 shows the comparisons of  $c_p^0$  calculated with Equation 7 to the values from TDE. For *n*-perfluorobutane, there are no experimental heat capacity data, but molecular simulation heat capacity data are introduced in section 4.2. For *n*-perfluoropentane and *n*-perfluorohexane, the paper of Cochran *et al.*<sup>42</sup> is the only publication containing isobaric heat capacity data, but fitting the data caused large deviations in other properties and were, thus, not used. Rather, the molecular simulation heat capacity data from the TDE program for *n*-perfluoropentane and *n*-perfluorobexane were used for fitting the ideal-gas isobaric heat capacity equations.

In the ideal-gas isobaric heat capacity equation of *n*-perfluorobutane, there are two Einstein-Planck terms, n = 2. The uncertainty of the ideal-gas isobaric heat capacity equation is 11 % as given in Table 7 and shown in Figure 2. The development of ideal-gas isobaric heat capacity equation is integrated with the whole fitting process, which is obtained by fitting not only the ideal-gas heat capacity data, but also the speed of sound and heat capacity data. Furthermore, the speed of sound and heat capacity data should be considered firstly. Hence, the large deviation in ideal-gas heat capacity of *n*-perfluorobutane is accepted. In the ideal-gas isobaric heat capacity equations of *n*-perfluorobecane, there are three Einstein-Planck terms, n = 3. For *n*-

perfluoropentane, although values of the ideal-gas isobaric heat capacity equation were fitted within 0.2 % to those available in the TDE program as shown in Figure 2, the uncertainty of approximately 2 %, is much higher due to the estimation methods used by TDE to obtain these values. Likewise, for *n*-perfluorohexane, the uncertainty of the ideal-gas isobaric heat capacity equation is estimated to be 2 %.

Table 6. Coefficients of ideal-gas isobaric heat capacity equations for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane

Substance	$c_0$	k	$v_k$	$u_k(\mathbf{K})$
" Darfluorobutana	14.0	1	2.164	368
<i>n</i> -remuorobutane	14.0	2	15.64	810
		1	5.761	485
n-Perfluoropentane	15.0	2	19.37	1026
_		3	7.096	2009
		1	4.902	433
n-Perfluorohexane	17.0	2	23.43	910
		3	10.52	1982

**Table 7.** Summary of sources of ideal-gas isobaric heat capacities for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane, and all those data are from TRC (Diky *et al.*<sup>10</sup>)

Substance	No. Points	Temperature Range T (K)	AAD %
<i>n</i> -Perfluorobutane	14	200-1500	11.05
n-Perfluoropentane	14	200-1500	0.05
n-Perfluorohexane	14	200-1500	0.10

When Equation 7 is substituted into Equation 6, the dimensionless ideal-gas Helmholtz energy can be expressed as

$$\alpha^{0}(\tau,\delta) = a_{1} + a_{2}\tau + \ln\delta + (c_{0}-1)\ln\tau + \sum_{k=1}^{n}v_{k}\ln\left[1 - \exp\left(-\frac{u_{k}\tau}{T_{c}}\right)\right].$$
(8)

In this work, the normal-boiling point for the saturated liquid state was selected as the reference state at which both the values of enthalpy and entropy are zero. Therefore, the values of  $h_0^0$  and  $s_0^0$  at  $T_0 = 273.15$  K and  $p_0 = 1.0$  kPa required to obtain this reference state were calculated from the final equation of this work. The values of  $h_0^0$  and  $s_0^0$  are given in Table 1, and the other coefficients in Equation 8 are the same with those in Equation 7. The resulting values of  $a_1$  and  $a_2$  are 7.00619051416 and -4.93953188697 for *n*-perfluorobutane, 9.47670389005 and -6.53756604064 for *n*-perfluoropentane, and 14.4861274604 and -9.80302171399 for *n*-perfluorohexane, respectively.



**Figure 2.** Comparisons of  $c_p^0$  values calculated with Equation 7 for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane to TDE<sup>10</sup> data.

#### 4.2. Molecular modeling and simulation

In order to complement the limited amount of experimental data for the fitted substances, molecular simulations were carried out. For *n*-perfluorobutane, a molecular force field of Köster *et al.*<sup>18</sup> was employed, which consists of 14 Lennard-Jones sites and 14 point charges, i.e., every atom of the molecule is represented by both site types. Although *n*-perfluorobutane is quite large, its intramolecular interactions were not modeled explicitly. Nonetheless, its performance is

satisfactory and allows for a prediction of thermodynamic properties over a large range of states.<sup>18</sup> VLE data generated with this force field were directly taken from the work of Köster *et al.*,<sup>18</sup> whereas new simulations were carried out for homogeneous thermodynamic properties.

For this purpose, the molecular simulation code  $ms2^{43-45}$  was employed. With the use of the Lustig-formalism,<sup>46, 47</sup> ms2 is able to sample partial residual Helmholtz energy derivatives in the *NVT* ensemble, where the number of particles *N*, the volume *V*, and the temperature *T* are held constant. These derivatives are given by

$$\frac{\partial^{m+n} a^{\mathrm{r}} / (RT)}{\partial (1/T)^{m} \partial \rho^{n}} (1/T)^{m} \rho^{n} = A^{\mathrm{r}}_{mn}$$

$$\tag{9}$$

and can be combined with the ideal-gas Helmholtz energy from the present equation of state (cf. section 4.1) to calculate every thermodynamic state property.<sup>48</sup> In the present work, this procedure was employed for the isochoric and isobaric heat capacities as well as the speed of sound and homogeneous densities.

Sixty eight state points over a wide range of temperatures (300 to 800 K) and densities (0.1 to 8 mol·dm<sup>-3</sup>) were simulated with Monte Carlo methods for *n*-perfluorobutane. Prior to the production phase of 10<sup>6</sup> cycles, where the Helmholtz energy derivatives were sampled, the 500 particles were equilibrated sufficiently. The cutoff radius was specified to be half of the edge length of the cubic simulation volume. All resulting numerical Helmholtz energy derivative data can be found in Table 8. The molecular simulation data of  $p\rho T$ , speed of sound, and isobaric and isochoric heat capacities for *n*-perfluorobutane are given in Table 9.

Table 8. Helmholtz energy derivatives for *n*-perfluorobutane with the associated statistical uncertainties obtained from molecular simulation<sup>a</sup>

<i>T</i> (K)	$\rho (\mathrm{mol}\cdot\mathrm{dm}^{-3})$	$A_{00}^{\mathrm{r}}$	$\Delta A_{00}^{\rm r}$	$A_{10}^{\mathrm{r}}$	$\Delta A_{10}^{\rm r}$	$A_{01}^{\mathrm{r}}$	$\Delta A_{01}^{\rm r}$	$A_{20}^{\mathrm{r}}$	$\Delta A_{20}^{\rm r}$	$A_{11}^{\mathrm{r}}$	$\Delta A_{11}^{\rm r}$	$A_{02}^{ m r}$	$\Delta A_{02}^{\rm r}$
800	0.1	0.00223	0.00006	-0.03323	0.00001	0.00256	0.00005	-0.01570	0.00003	-0.03328	0.00018	0.00025	0.00183
800	1.0	0.03803	0.00026	-0.33386	0.00006	0.05465	0.00022	-0.13182	0.00040	-0.33744	0.00195	0.04819	0.01640
800	2.0	0.11535	0.00047	-0.67921	0.00013	0.19655	0.00037	-0.21467	0.00086	-0.70908	0.00342	0.23417	0.03671
800	3.0	0.24594	0.00080	-1.05054	0.00014	0.49042	0.00059	-0.27250	0.00105	-1.15313	0.00572	0.74889	0.06822
800	4.0	0.45705	0.00168	-1.46027	0.00011	1.06465	0.00097	-0.33471	0.00090	-1.73257	0.00752	2.10688	0.10983
800	5.0	0.80672	0.00444	-1.91012	0.00010	2.16664	0.00120	-0.44271	0.00118	-2.35898	0.01403	5.01424	0.17403
800	6.0	1.38362	0.02437	-2.38121	0.00014	4.25379	0.00207	-0.64533	0.00201	-2.82949	0.02331	12.28470	0.30487
800	7.0	2.78457	0.33309	-2.81273	0.00026	8.10929	0.00375	-0.98411	0.00381	-2.61617	0.04607	28.10912	0.58487
800	8.0	23.42212	0.99387	-3.07868	0.00070	15.00496	0.00809	-1.52864	0.00802	-1.02089	0.08911	56.24401	1.00753
700	0.1	-0.00230	0.00007	-0.04060	0.00001	-0.00256	0.00006	-0.02164	0.00004	-0.04068	0.00022	0.00145	0.00180
700	1.0	-0.01143	0.00028	-0.40361	0.00008	0.00533	0.00024	-0.18183	0.00069	-0.40105	0.00202	0.05267	0.01721
700	2.0	0.01516	0.00060	-0.81160	0.00019	0.09351	0.00052	-0.28462	0.00138	-0.83751	0.00423	0.20489	0.04408
700	3.0	0.09249	0.00086	-1.24394	0.00019	0.32183	0.00062	-0.34002	0.00159	-1.33979	0.00657	0.79925	0.07083
700	4.0	0.24771	0.00175	-1.71952	0.00022	0.81426	0.00108	-0.38537	0.00151	-2.01894	0.01016	1.83295	0.11786
700	5.0	0.52561	0.00433	-2.24866	0.00013	1.82503	0.00144	-0.47547	0.00133	-2.75253	0.01293	5.44309	0.18142
700	6.0	1.05197	0.03199	-2.81492	0.00012	3.84126	0.00190	-0.67102	0.00200	-3.41368	0.02372	13.01123	0.33908
700	7.0	2.26128	0.50558	-3.35756	0.00023	7.70776	0.00302	-1.01168	0.00326	-3.35424	0.03896	29.86784	0.53743
700	8.0	35.81105	0.99387	-3.73939	0.00061	14.82734	0.00699	-1.57771	0.00955	-1.76439	0.10476	61.52001	1.21072
600	0.1	-0.00977	0.00007	-0.05179	0.00002	-0.00935	0.00006	-0.03259	0.00006	-0.05182	0.00028	-0.00286	0.00229
600	1.0	-0.08150	0.00031	-0.50795	0.00013	-0.06370	0.00024	-0.27698	0.00110	-0.50084	0.00322	0.04835	0.02273
600	2.0	-0.12534	0.00058	-1.00512	0.00024	-0.04624	0.00047	-0.42407	0.00288	-1.00417	0.00657	0.20835	0.04638
600	3.0	-0.11999	0.00100	-1.51786	0.00033	0.09549	0.00075	-0.46663	0.00288	-1.61357	0.00810	0.61284	0.08028
600	4.0	-0.04945	0.00208	-2.07810	0.00025	0.47977	0.00118	-0.48163	0.00239	-2.37389	0.01090	1.95716	0.14559
600	5.0	0.15853	0.00555	-2.70723	0.00019	1.35559	0.00169	-0.53796	0.00182	-3.35667	0.01572	4.53557	0.24139
600	6.0	0.51123	0.02948	-3.39898	0.00014	3.24977	0.00245	-0.71265	0.00168	-4.28402	0.01849	12.47194	0.29943
600	7.0	2.01764	0.27987	-4.09068	0.00024	7.08927	0.00352	-1.05886	0.00412	-4.50427	0.04913	30.27089	0.64631
600	8.0	105.02262	0.97145	-4.63278	0.00061	14.44325	0.00785	-1.65703	0.00949	-3.06387	0.10336	65.20957	1.18561
500	0.1	-0.02065	0.00009	-0.07064	0.00002	-0.02062	0.00008	-0.05543	0.00014	-0.07114	0.00037	0.00347	0.00306
500	1.0	-0.18918	0.00041	-0.68238	0.00029	-0.16801	0.00034	-0.49557	0.00330	-0.64774	0.00431	0.04411	0.02994
500	2.0	-0.33611	0.00073	-1.31820	0.00051	-0.25025	0.00052	-0.75239	0.00758	-1.25389	0.01041	0.13545	0.05759
500	3.0	-0.43690	0.00145	-1.94088	0.00072	-0.22238	0.00090	-0.78833	0.00901	-1.86344	0.01495	0.62302	0.09829
500	4.0	-0.47464	0.00287	-2.60775	0.00057	0.00481	0.00159	-0.70569	0.00599	-2.82197	0.01745	1.63894	0.15228
500	5.0	-0.40312	0.00693	-3.36648	0.00034	0.68021	0.00173	-0.65265	0.00295	-4.08199	0.01984	4.45312	0.24455
500	6.0	-0.12692	0.03288	-4.22666	0.00021	2.37964	0.00222	-0.77625	0.00228	-5.42971	0.02675	11.64624	0.45541
500	7.0	0.70917	0.39624	-5.12730	0.00028	6.12612	0.00457	-1.12357	0.00395	-6.13324	0.05044	30.62128	0.77757

<i>T</i> (K)	$\rho$ (mol·dm <sup>-3</sup> )	$A_{00}^{ m r}$	$\Delta A_{00}^{\rm r}$	$A_{10}^{\mathrm{r}}$	$\Delta A_{10}^{\rm r}$	$A_{01}^{\mathrm{r}}$	$\Delta A_{01}^{\rm r}$	$A_{20}^{\mathrm{r}}$	$\Delta A_{20}^{\rm r}$	$A_{11}^{\mathrm{r}}$	$\Delta A_{11}^{\rm r}$	$A_{02}^{ m r}$	$\Delta A_{02}^{\rm r}$
500	8.0	69.87735	0.99388	-5.89977	0.00070	13.72547	0.00890	-1.73756	0.01068	-4.78193	0.12553	70.28616	1.57725
450	0.1	-0.02895	0.00010	-0.08577	0.00003	-0.02873	0.00009	-0.07730	0.00018	-0.08603	0.00051	-0.00547	0.00375
450	1.0	-0.26854	0.00046	-0.82497	0.00046	-0.24396	0.00035	-0.73862	0.00562	-0.78086	0.00616	0.10572	0.02835
450	2.0	-0.48859	0.00090	-1.56820	0.00105	-0.38998	0.00058	-1.16686	0.01762	-1.42544	0.01318	0.26319	0.07284
450	3.0	-0.65696	0.00188	-2.26227	0.00125	-0.43334	0.00120	-1.16716	0.01722	-2.07083	0.02317	0.42922	0.11811
450	4.0	-0.76690	0.00337	-2.98739	0.00079	-0.30554	0.00162	-0.92192	0.01316	-3.10513	0.02622	1.34357	0.16189
450	5.0	-0.77463	0.00802	-3.82120	0.00042	0.23849	0.00202	-0.78378	0.00480	-4.46027	0.02494	4.47122	0.27107
450	6.0	-0.67188	0.04537	-4.78612	0.00024	1.76813	0.00299	-0.83143	0.00287	-6.08603	0.03353	12.50527	0.43396
450	7.0	1.50340	0.59676	-5.82444	0.00030	5.41567	0.00503	-1.16011	0.00497	-7.14232	0.05983	31.83604	0.82823
450	8.0	119.73342	0.99389	-6.75239	0.00068	13.15460	0.00945	-1.80830	0.00954	-6.09194	0.11477	73.30972	1.47177
400	0.1	-0.04032	0.00013	-0.10831	0.00003	-0.04003	0.00010	-0.11531	0.00033	-0.10832	0.00077	0.00001	0.00394
400	1.0	-0.37877	0.00077	-1.05169	0.00096	-0.34746	0.00058	-1.35054	0.01968	-0.99614	0.01107	0.06822	0.03865
400	2.0	-0.69669	0.00166	-1.97424	0.00316	-0.57123	0.00086	-2.31289	0.07664	-1.63634	0.02836	0.17088	0.09739
400	3.0	-0.95704	0.00274	-2.73740	0.00230	-0.68806	0.00141	-1.91186	0.04465	-2.33835	0.03230	0.67868	0.13594
400	4.0	-1.14948	0.00481	-3.50892	0.00199	-0.68111	0.00231	-1.47721	0.03209	-3.27297	0.03712	1.39586	0.19558
400	5.0	-1.26979	0.00866	-4.40710	0.00067	-0.32294	0.00223	-1.00362	0.00872	-4.96620	0.03480	3.37076	0.30996
400	6.0	-1.19822	0.04250	-5.49321	0.00034	0.99801	0.00271	-0.91746	0.00386	-7.01719	0.02985	11.74284	0.48679
400	7.0	0.05981	0.67073	-6.70084	0.00030	4.50120	0.00492	-1.21064	0.00557	-8.41785	0.06011	33.72865	0.81519
400	8.0	85.88290	0.99390	-7.83060	0.00085	12.29934	0.01059	-1.87776	0.01137	-7.66073	0.13418	77.70019	1.71117
350	0.1	-0.05720	0.00016	-0.14488	0.00007	-0.05664	0.00014	-0.19002	0.00055	-0.14490	0.00117	0.00425	0.00542
350	0.2	-0.11364	0.00027	-0.29111	0.00013	-0.11277	0.00021	-0.40628	0.00125	-0.29667	0.00263	-0.01064	0.01214
350	0.3	-0.17033	0.00039	-0.43848	0.00018	-0.16678	0.00029	-0.65081	0.00306	-0.44994	0.00467	-0.00802	0.01766
350	0.4	-0.22621	0.00045	-0.58701	0.00035	-0.22006	0.00032	-0.92411	0.00650	-0.60870	0.00602	-0.00348	0.02462
350	6.0	-2.01575	0.06563	-6.41861	0.00055	-0.01249	0.00406	-1.06155	0.00573	-8.11324	0.04220	10.13722	0.56758
350	6.5	-1.99091	0.16398	-7.11362	0.00033	1.22651	0.00437	-1.11335	0.00511	-9.21560	0.04820	19.90240	0.80712
350	7.0	-2.92845	0.60902	-7.83769	0.00036	3.25772	0.00536	-1.29386	0.00548	-10.22820	0.05627	31.79617	0.80940
350	7.5	2.04932	0.99387	-8.55705	0.00046	6.41094	0.00765	-1.56992	0.00790	-10.42953	0.09776	53.34103	1.38989
350	8.0	118.34219	0.99301	-9.22456	0.00081	11.12225	0.01217	-1.98002	0.01384	-10.01343	0.16302	77.80805	2.11897
300	0.1	-0.08434	0.00023	-0.21355	0.00012	-0.08425	0.00018	-0.37827	0.00173	-0.21542	0.00231	-0.00380	0.00701
300	6.5	-3.37987	0.25700	-8.49697	0.00050	-0.34075	0.00526	-1.29668	0.00803	-11.20393	0.05594	18.03877	0.87995
300	7.0	-2.53280	0.45558	-9.36706	0.00042	1.51940	0.00540	-1.39498	0.00609	-12.31572	0.06420	32.44257	0.95799
300	7.5	7.89027	0.99115	-10.25389	0.00054	4.59621	0.00813	-1.68269	0.01014	-13.28725	0.11922	51.54796	1.57834
300	8.0	213.18353	0.99396	-11.09960	0.00104	9.39272	0.01535	-2.11229	0.01601	-13.03251	0.21604	81.21870	3.00606

<sup>a</sup>The residual properties are calculated from the molecular simulation in section 4.2 and the ideal-gas properties are calculated from the ideal-gas Helmholtz energy equation in section 4.1.

Temperature T	Density $\rho$	Pressure p	Speed of Sound w	Isobaric Heat	Isochoric Heat
K	mol·dm <sup>-3</sup>	kPa	$m \cdot s^{-1}$	Capacity $c_p$	Capacity $c_v$
				J·mol <sup>-1</sup> ·K <sup>-1</sup>	J·mol <sup>-1</sup> ·K <sup>-1</sup>
800	0.1	666.867	170.618	254.247	245.373
800	1	7015.11	184.859	260.259	246.339
800	2	15918.0	221.108	265.582	247.028
800	3	29741.1	287.820	268.794	247.508
800	4	54933.0	399.785	270.921	248.026
800	5	105316	563.606	273.457	248.923
800	6	209677	818.258	275.537	250.608
800	7	424140	1180.13	278.644	253.425
800	8	851670	1642.97	285.575	257.952
700	0.1	580.524	158.951	251.295	242.302
700	1	5851.18	166.283	259.100	243.634
700	2	12728.8	192,703	266.763	244.489
700	3	23079.7	256.148	269.060	244,949
700	4	42237.2	348 231	272 709	245 326
700	5	82210.5	522.007	271.702	246.075
700	6	169061	765 746	273.819	247 701
700	7	354764	1117.92	275.670	250 534
700	8	7360/1	1581.23	270.070	255.240
700 600	0 1	/ 30941	1301.25	265.155	233.240
600	0.1	494.200	143.933	240.999	237.704
600	1	40/0.95	144.230	230.442	239.790
600	2	9510.04	101./34	209.385	241.019
600	3	16395.2	207.613	275.201	241.3/3
600	4	29528.5	304.635	273.023	241.497
600	2	58/56.8	443.098	2/4.863	241.966
600	6	127205	686.076	2/3./3/	243.418
600	7	282485	1031.87	275.310	246.297
600	8	616335	1493.51	281.217	251.270
500	0.1	407.152	132.288	240.261	230.725
500	1	3458.79	117.147	260.096	234.385
500	2	6233.82	116.423	289.089	236.520
500	3	9698.29	157.657	286.040	236.819
500	4	16708.9	235.081	282.104	236.132
500	5	34925.3	373.439	276.208	235.691
500	6	84300.1	592.955	273.790	236.719
500	7	207376	934.242	272.924	239.607
500	8	489740	1396.52	276.756	244.712
450	0.1	363.405	124.004	235.631	225.713
450	1	2828.75	105.101	263.000	231.211
450	2	4564.79	99.5083	306.059	234.772
450	3	6360.50	112.759	337.591	234.774
450	4	10393.4	187.988	302.020	232.735
450	5	23169.2	334.402	276.982	231.587
450	6	62142.3	558.602	270.232	231.983
450	7	168031	888.113	269.715	234.715
450	8	423679	1343.40	273.978	240.105
400	0.1	319.267	116.010	229.554	219.240
400	1	2170.22	81.1887	290.051	229.510
400	2	2852.00	49.8296	1485.24	237.511
400	3	3112.34	87.8171	427.203	234.177
400	4	4242.26	144.716	334.341	230.563
400	5	11258.8	261 475	297 711	226.626
400	6	39869 9	497 722	271 757	225.909
400	7	128072	842 366	265 182	228.347
400	8	353848	1289.00	269 254	233 894
350	0.1	274 525	107.068	207.204	210.856
350	0.2	516 383	107.000	227.900	210.050
350	0.2	777 171	03 06/10	227.911	212.034
550	0.5	121.727	75.70	233.717	217.00/

**Table 9.** Molecular simulation data of  $p\rho T$ , speed of sound, and isobaric and isochoric heat capacities for *n*-perfluorobutane calculated from the Helmholtz energy derivatives in Table 8

Temperature T	Density $\rho$	Pressure p	Speed of Sound w	Isobaric Heat	Isochoric Heat
K	mol∙dm <sup>-3</sup>	kPa	$\mathbf{m} \cdot \mathbf{s}^{-1}$	Capacity $c_p$	Capacity $c_v$
				$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$
350	0.4	907.869	87.7816	245.775	216.959
350	6	17242.4	417.678	280.073	218.102
350	6.5	42115.6	588.585	265.140	218.533
350	7	86732.1	759.967	264.415	220.033
350	7.5	161748	983.172	261.731	222.329
350	8	282214	1206.68	266.054	225.738
300	0.1	228.419	96.0722	213.203	200.350
300	6.5	10688.6	501.322	271.728	207.986
300	7	43990.0	688.568	258.962	208.803
300	7.5	104692	891.118	259.216	211.195
300	8	207385	1131.83	259.939	214.767

#### 4.3. Properties of the real fluid

Compared with the ideal-gas Helmholtz energy function, the formulation of the residual part is more complex and can be represented as

$$\alpha^{\mathrm{r}}(\tau,\delta) = \sum_{i=1}^{5} n_i \delta^{d_i} \tau^{t_i} + \sum_{i=6}^{9} n_i \delta^{d_i} \tau^{t_i} \exp\left(-\delta^{t_i}\right) + \sum_{i=10}^{14} n_i \delta^{d_i} \tau^{t_i} \exp\left[-\eta_i \left(\delta - \varepsilon_i\right)^2 - \beta_i \left(\tau - \gamma_i\right)^2\right],$$
(10)

where the first two summations contain five polynomial and four exponential terms, respectively, and the index *i* points to each individual term. The coefficients and exponents of Equation 10 for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane are given in Table 10. The temperature, pressure, and density ranges of the equations of state for these fluids have already been listed in Table 1. All thermodynamic properties can be calculated from Equations 8 and 10 as explained by Lemmon *et al.*<sup>49</sup> When developing an equation of state, the values of  $t_i$  should be greater than zero, and  $d_i$  and  $l_i$  should be integers greater than zero.<sup>40</sup> The third summation contains five Gaussian bell-shaped terms, which are extremely sensitive but powerful in modeling the properties of fluids in the critical region, especially for densities, and are applied to all fluid phase regions.

i	ni	ti	$d_i$	li	$\eta_i$	$\beta_i$	γi	Ei
			n-I	Perfluorobuta	ine			
1	0.025377604	1.0	4					
2	0.97089776	0.135	1					
3	-0.76128126	1.0	1					
4	-1.2517125	1.0	2					
5	0.28005904	0.42	3					
6	-1.7144149	1.62	1	2				
7	-0.64918553	2.35	3	2				
8	1.1662335	1.01	2	1				
9	-0.35934725	2.65	2	2				
10	1.4986537	0.75	1		1.431	1.544	1.265	0.781
11	-0.60326234	1.28	1		1.803	1.366	1.156	0.723
12	-0.11389713	1.5	3		1.608	0.876	0.916	0.842
13	-0.2553212	1.0	2		1.837	1.117	0.927	0.652
14	-0.1017598	1.9	2		1.846	1.29	0.926	1.139
			n-P	erfluoropent	ane			
1	0.036359237	1.0	4	-				
2	1.1222855	0.19	1					
3	-0.63721964	1.0	1					
4	-1.3599906	1.0	2					
5	0.24995429	0.33	3					
6	-2.291332	1.51	1	2				
7	-0.95997986	2.22	3	2				
8	1.2463966	0.97	2	1				
9	-0.41785522	2.54	2	2				
10	-0.49360387	0.75	1		1.168	2.13	1.14	0.317
11	1.8336733	0.375	1		0.944	2.13	1.185	0.702
12	-0.27152337	0.5	1		2.28	2.13	0.95	0.686
13	-0.11731069	1.0	3		1.486	1.865	1.02	1.257
14	-0.488446	0.815	2		1.78	1.59	1.025	0.947
			n-H	Perfluorohexa	ine			
1	0.035689273	1.0	4					
2	0.89834616	0.146	1					
3	-0.11619207	1.0	1					
4	-1.6558707	1.0	2					
5	0.3090401	0.39	3					
6	-3.0212885	1.56	1	2				
7	-1.309987	2.25	3	2				
8	1.4611604	0.987	2	1				
9	-0.63849402	2.602	2	2				
10	-0.40480926	1.87	1		0.8775	1.171	1.254	0.36
11	2.3673483	0.97	1		1.0	1.14	1.312	0.755
12	0.40072213	2.22	1		1.327	0.645	1.178	1.693
13	-0.43534683	1.7	3		1.102	0.658	1.326	1.04
14	-0.90267664	1.31	2		1.274	0.727	0.902	0.646

Table 10. Coefficients of the equations of state for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane

The temperature exponents of the third, fourth, and eighth terms strongly influence the behavior of equations of state at very low temperatures, especially the third and fourth ones. When the temperature exponents of the third and fourth terms are exactly one, the low temperature behavior is more easily controlled for heat capacities, the phase identification parameter (PIP), and the Grüneisen parameter, which will be discussed in the subsequent sections. At the same time, the temperature exponent of the eighth term is always near to one. The temperature exponent of the second term determines the rate of descent towards zero of the second virial coefficient as temperature goes to infinity, which is larger with higher temperature exponents. The paper describing the R125 equation of state<sup>40</sup> pointed out that the term with  $d_i = 4$  and  $t_i = 1$  in the first summation makes the isotherms at high temperatures and pressures closer, without crossing with an increase of pressure and density. The fifth term also has influence in that region. With a decreasing temperature exponent, isotherms at high temperatures and pressures are more parallel, which they should not be.

# 5. Experimental Data and Comparisons to Equations of State

The data used to fit the equations of state for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane included saturation properties,  $p\rho T$ , heat capacities, speed of sound, and virial coefficients. If necessary, those data were converted to the ITS-90 temperature scale and molar SI-units, and are summarized in Tables 11 to 13. There are only a few experimental data in a limited state region for these three fluids. Therefore, additional data for *n*-perfluorobutane were determined from molecular simulation. These data were used to verify that the equation of state did not depart significantly from the actual properties without experimental data by being fitted with smaller weights than existing experimental data. This work compared all available data to the values calculated from the equations of state, including those not used in the development of the equations. The extrapolation behavior of the equations of state both within the region of validity and outside the region of validity at high temperatures and pressures, and at low temperatures is also analyzed.

The uncertainties of the equation of state were determined by statistical comparisons of calculated property values to experimental data. These statistics are based on the percent deviation

in any property *X*, defined as

$$\Delta X \% = 100 \left( \frac{X_{\exp} - X_{calc}}{X_{\exp}} \right).$$
(11)

With this definition, the average absolute relative deviation (AAD) is defined as

$$AAD = \frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} |\Delta X_i \%|, \qquad (12)$$

where  $N_{exp}$  is the number of experimental data points for each reference.

	Table 11.	Summary o	f sources o	ofext	perimental	data	for <i>n</i> -	perfluorobutane
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No. Temperature Pressure Range Density Range						
Reference	Points	Range T (K)	p (MPa)	$\rho (\mathrm{mol}\cdot\mathrm{dm}^{-3})$	%	
		Vapor Pressure				
Brown and Mears (1958) <sup>7</sup>	13	233-383	0.017-2.18		0.66	
Fowler <i>et al.</i> $(1947)^{17}$	13	245-363	0.035-1.39		3.1	
Gilmour <i>et al.</i> $(1967)^{15}$	1	271	0.101		0.32	
Köster <i>et al</i> . $(2012)^{18}$	4	268-298	0.091-0.269		0.76	
Köster et al. (2012) <sup>18</sup> (Simulation Data)	9	190-358	0.0007-1.29		10.	
Subramoney et al. (2013) <sup>50</sup>	17	303-343	0.316-0.919		0.83	
Valtz and Coquelet (2012) <sup>20</sup>	25	263-379	0.073-2		0.077	
	Satu	irated Liquid Densi	ity			
Brown and Mears (1958) <sup>7</sup>	7	233-347		5.29-7.24	0.12	
Fowler <i>et al.</i> $(1947)^{17}$	5	318-358		5-5.92	0.23	
Köster et al. (2012) <sup>18</sup> (Simulation Data)	9	190-358		4.91-7.84	0.57	
	Satu	irated Vapor Densi	ity			
Brown and Mears (1958) <sup>7</sup>	7	233-347		0.008-0.496	1.7	
Fowler <i>et al.</i> $(1947)^{17}$	5	318-358		0.223-0.618	5.4	
Köster et al. (2012) <sup>18</sup> (Simulation Data)	9	190-358		0.0008-0.633	14.	
		$p \rho T$				
Brown and Mears (1958) <sup>7</sup>	46	338-455	0.698-5.4	0.307-2.62	1.1	
Simulation Data (this work)	68	300-800	0.228-852	0.1-8	2.8	
		Speed of Sound				
Hallewell <i>et al.</i> $(2010)^{51}$	38	248-303	0.01-0.3		0.18	
Simulation Data (this work)	68	300-800		0.1-8	8.2	
Vacek <i>et al.</i> (2001) <sup>52</sup>	38	255-303	0.01-0.3		0.42	
	Iso	baric Heat Capacit	у			
Simulation Data (this work)	68	300-800		0.1-8	2.4	
	Iso	choric Heat Capaci	ty			
Simulation Data (this work)	68	300-800		0.1-8	0.70	
	Н	eat of Vaporization	l			
Köster et al. (2012) <sup>18</sup> (Simulation Data)	9	190-358			3.5	
	Seco	ond Virial Coefficie	ent			
Dantzler and Knobler (1969) <sup>53</sup>	2	323-373			37.	
Köster et al. (2012) <sup>18</sup> (Simulation Data)	9	190-358			14.	
Tripp and Dunlap (1962) <sup>54</sup>	3	283-323			96.	

	Table 12. Summ	ary of source	es of expe	erimental o	data for <i>n</i> -	perfluoror	bentane
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	No.	Temperature Range	Pressure Range	Density Range	$AAD^{a}$
Reference	Points	$T(\mathbf{K})$	p (MPa)	$\rho (\mathrm{mol} \cdot \mathrm{dm}^{-3})$	%
		Vapor Pressure			
Aftienjew and Zawisza (1977) <sup>28</sup>	6	333-403	0.277-1.46		0.10
Barber and Cady (1951) <sup>55</sup>	2	298-314	0.086-0.152		0.20
Barber and Cady (1956) <sup>26</sup>	17	283-338	0.046-0.319		0.42

Crowder et al. (1967) <sup>25</sup>	14	221-303	0.001-0.104		0.98
Ermakov and Skripov (1967) <sup>29</sup>	10	300-422	0.1-2.04		2.2
Simons and Dunlap (1950) <sup>3</sup>	5	262-293	0.02-0.075		8.0
	Sa	turated Liquid Der	nsity		
Aftienjew and Zawisza (1977) <sup>28</sup>	6	333-403	•	3.76-5.14	0.13
Burger <i>et al.</i> (1951) <sup>24</sup>	20	185-303		5.5-6.72	0.079
Cochran <i>et al.</i> (1974) <sup>42</sup>	5	233-253		6.14-6.4	1.8
Ermakov and Skripov (1969) <sup>30</sup>	4	313-403		3.78-5.38	0.35
•	Sa	turated Vapor Den	sity		
Aftienjew and Zawisza (1977) <sup>28</sup>	6	333-403	•	0.114-0.762	2.9
Ermakov and Skripov (1969) <sup>30</sup>	4	313-403		0.055-0.733	4.1
<b>*</b> • • •		pρT			
Aftienjew and Zawisza (1977) <sup>28</sup>	115	333-504	0.197-4.49	0.052-5.29	0.77
5		Speed of Sound			
Cochran <i>et al.</i> (1974) <sup>42</sup>	5	233-253	0.101		4.0
	Is	obaric Heat Capac	city		
Cochran <i>et al.</i> (1974) <sup>42</sup>	3	233-253	0.101		34.
	Se	cond Virial Coeffic	eient		
Dantzler and Knobler (1969) <sup>53</sup>	2	323-373			42.
Garner and McCoubrey (1959) <sup>56</sup>	6	308-383			32.

Table 13. Summar	ry of sources	of ex	perimental	data for n-	perfluorohexane
	- /				

	No.	Temperature	Pressure Range	Density Range	$AAD^{a}$
Reference	Points	Range T (K)	p (MPa)	$\rho (\mathrm{mol}\cdot\mathrm{dm}^{-3})$	%
		Vapor Pressure			
Alekseeva et al. (1985)57	4	298-318	0.03-0.066		0.55
Crowder et al. (1967) <sup>25</sup>	20	256-447	0.003-1.7		0.85
Dias <i>et al.</i> $(2005)^{58}$	10	288-333	0.019-0.111		0.072
Dunlap <i>et al.</i> (1958) <sup>32</sup>	9	303-331	0.036-0.102		0.13
Ermakov and Skripov (1967) <sup>29</sup>	16	324-452	0.1-1.91		6.9
Mousa (1978) <sup>36</sup>	12	433-449	1.36-1.87		4.3
Stiles and Cady (1952) <sup>34</sup>	18	284-342	0.015-0.149		0.39
	S	aturated Liquid Densi	ity		
Cochran <i>et al.</i> (1974) <sup>42</sup>	9	233-273		5.15-5.41	1.0
Dias <i>et al.</i> $(2005)^{58}$	5	288-313		4.82-5.05	0.038
Dunlap <i>et al.</i> (1958) <sup>32</sup>	4	288-318		4.76-5.03	0.29
Ermakov and Skripov (1969) <sup>30</sup>	6	293-433		3.17-4.97	1.0
Hallewell et al. (2010) <sup>51</sup>	4	278-308		4.89-5.15	0.40
Kennan and Pollack (1988) <sup>59</sup>	5	278-298		4.96-5.12	0.13
Stiles and Cady (1952) <sup>34</sup>	10	273-323		4.75-5.19	0.46
Taylor et al. (1970) <sup>39</sup>	4	396-448		2.54-3.91	4.1
TRC (Diky <i>et al.</i> <sup>10</sup> )	3	288-298		4.94-5.05	0.14
	S	aturated Vapor Densi	ty		
Ermakov and Skripov (1969) <sup>30</sup>	5	313-433		0.019-0.638	6.9
Taylor <i>et al.</i> (1970) <sup>39</sup>	4	396-448		0.243-1.06	20.
		ррТ			
Dunlap <i>et al.</i> (1958) <sup>32</sup>	4	288-318	0.101	4.76-5.03	0.44
Piñeiro et al. (2004)60	100	283-313	0.1-40	4.82-5.42	0.045
Strejc <i>et al.</i> (2014) <sup>61</sup>	11	278-328	0.1	4.71-5.15	0.45
		Speed of Sound			
Cochran <i>et al</i> . (1974) <sup>42</sup>	9	233-273	0.101		2.4
Hallewell et al. $(2010)^{51}$	3	278-298	0.101		0.61
	]	sobaric Heat Capacit	у		
Cochran <i>et al</i> . (1974) <sup>42</sup>	5	233-273	0.101		60.
		Heat of Vaporization	L		
Dunlap <i>et al</i> . (1958) <sup>32</sup>	1	330			1.1
	S	econd Virial Coefficie	nt		
Cecil (1964) <sup>62</sup>	4	303-351			220.
Dantzler and Knobler (1969) <sup>53</sup>	2	323-373			45.
Dunlap <i>et al.</i> (1958) <sup>32</sup>	1	303			1038.
Garner and McCoubrey (1959) <sup>56</sup>	6	308-384			55.
Taylor <i>et al.</i> (1970) <sup>39</sup>	7	341-452			19.

		Third Virial Coefficient	
Taylor <i>et al.</i> (1970) <sup>39</sup>	4	396-452	58.

<sup>*a*</sup>The unit of AAD in Tables 12-14 for second virial coefficients is  $cm^3 \cdot mol^{-1}$ , and for third virial coefficients is  $10^3 \cdot cm^6 \cdot mol^{-2}$ .

#### 5.1. Comparisons with saturation data

### 5.1.1. *n*-perfluorobutane

Figures 3 to 5 compare vapor pressures, saturated liquid densities, and saturated vapor densities calculated from the equation of state for *n*-perfluorobutane to experimental data and molecular simulation data based on the methods from Köster *et al.*<sup>18</sup> Table 11 gives the AADs of these three saturation properties. The AADs in vapor pressure for the different datasets are Brown and Mears,<sup>7</sup> 0.66 %, Fowler et al.,<sup>17</sup> 3.08 %, Gilmour et al.,<sup>15</sup> 0.32 %, the experimental data from Köster et al.,<sup>18</sup> 0.76 %, the molecular simulation data from Köster et al.,<sup>18</sup> 10.1 %, Subramoney et al.,<sup>50</sup> 0.83 %, and Valtz and Coquelet,<sup>20</sup> 0.077 %, respectively. Figure 3 shows that there are no experimental data for vapor pressure at temperatures below 230 K, and most of the data are located at temperatures between 270 K and 360 K. Only Brown and Mears<sup>7</sup> and Fowler et al.<sup>17</sup> reported vapor pressures at temperatures between 230 K and 260 K. They significantly differ from each other at higher temperatures and even are not even consistent with their own data. The dataset of Fowler et al.<sup>17</sup> has large deviations of about 10 % as shown in Figure 3. The data from Valtz and Coquelet<sup>20</sup> are located at temperatures between 260 K and 380 K, and can be fitted to agree well with vapor pressures calculated from the equation of state, but not with the other datasets. The deviations of most data from Valtz and Coquelet<sup>20</sup> are within  $\pm 0.2$  %, so the uncertainty in vapor pressure of the equation of state is generally estimated to be 0.2 % at temperatures between 260 K and 380 K. Both the experimental saturated liquid and vapor density data are from the same two datasets, Brown and Mears<sup>7</sup> and Fowler et al.,<sup>17</sup> and are located at temperatures between 230 K and 360 K. The AADs in saturated liquid density for the datasets of Brown and Mears,<sup>7</sup> Fowler et al.,<sup>17</sup> and Köster et al. (simulation data)<sup>18</sup> are 0.12 %, 0.23 %, and 0.57 %, respectively. Figure 4

displays that the deviations of most experimental saturated liquid density data are within  $\pm 0.2$  %. The AADs in saturated vapor density for the datasets of Brown and Mears,<sup>7</sup> Fowler *et al.*,<sup>17</sup> and Köster *et al.* (simulation data)<sup>18</sup> are 1.73 %, 5.4 %, and 14.4 %, respectively. As shown in Figure 5, these two datasets deviate from each other at temperatures higher than 325 K; the deviations of most of the data from Brown and Mears<sup>7</sup> are within  $\pm 2$  %.



**Figure 3.** Comparisons of vapor pressures calculated with the equation of state for *n*-perfluorobutane to experimental and simulated data.



Figure 4. Comparisons of saturated liquid densities calculated with the equation of state for *n*-perfluorobutane to experimental and simulated data.



Figure 5. Comparisons of saturated vapor densities calculated with the equation of state for *n*-perfluorobutane to experimental and simulated data.

# 5.1.2. *n*-perfluoropentane

Figures 6 to 8 compare vapor pressures, saturated liquid densities, and saturated vapor densities calculated from the equation of state for *n*-perfluoropentane to experimental data. These are summarized in Table 12, which also gives the AADs of all these three saturation properties. The AADs in vapor pressure are Aftieniew and Zawisza,<sup>28</sup> 0.10 %, Barber and Cady,<sup>55</sup> 0.20 %, Barber and Cady,<sup>26</sup> 0.42 %, Crowder et al.,<sup>25</sup> 0.98 %, Ermakov and Skripov,<sup>29</sup> 2.2 %, and Simons and Dunlap,<sup>3</sup> 8.0 %, respectively. As shown in Figure 6, there is no data for vapor pressure at temperatures below 220 K, and the data from Ermakov and Skripov<sup>29</sup> and Simons and Dunlap<sup>3</sup> do not agree well with the other datasets. The data from Barber and Cady<sup>26</sup> at temperatures between 280 K and 315 K and the data from Aftienjew and Zawisza<sup>28</sup> can be fitted to agree very well with the values calculated from the equation of state; the deviations are within  $\pm 0.1$  %. The AADs in saturated liquid density for the datasets of Aftienjew and Zawisza,<sup>28</sup> Burger et al.,<sup>24</sup> Cochran et al.<sup>42</sup> and Ermakov and Skripov<sup>30</sup> are 0.13 %, 0.079 %, 1.8 %, and 0.35 %, respectively. As shown in Figure 7, the data from Cochran et al.<sup>42</sup> depart significantly from the other datasets. The deviations of the other saturated liquid density data are within  $\pm 0.3$  %. The AADs in saturated vapor density for the datasets of Aftienjew and Zawisza<sup>28</sup> and Ermakov and Skripov<sup>30</sup> are 2.9 %

and 4.1 %, respectively. As shown in Figure 8, the data are available only at temperatures higher than 310 K, and the deviations of most of the saturated vapor density data are within  $\pm 2$  %.



Figure 6. Comparisons of vapor pressures calculated with the equation of state for *n*-perfluoropentane to experimental data.



**Figure 7.** Comparisons of saturated liquid densities calculated with the equation of state for *n*-perfluoropentane to experimental data.



**Figure 8.** Comparisons of saturated vapor densities calculated with the equation of state for *n*-perfluoropentane to experimental data.

# 5.1.3. *n*-perfluorohexane

Figures 9 to 11 compare vapor pressures, saturated liquid densities, and saturated vapor densities calculated from the equation of state for *n*-perfluorohexane to experimental data. Summaries are given in Table 13, along with the AADs of all these three saturation properties. The AADs in vapor pressure are Alekseeva et al.,<sup>57</sup> 0.55 %, Crowder et al.,<sup>25</sup> 0.85 %, Dias et al.,<sup>58</sup> 0.072 %, Dunlap et al.,<sup>32</sup> 0.13 %, Ermakov and Skripov,<sup>29</sup> 6.9 %, Mousa,<sup>36</sup> 4.3 %, and Stiles and Cady,<sup>34</sup> 0.39 %, respectively. Figure 9 shows that the data from Ermakov and Skripov<sup>29</sup> and Mousa<sup>36</sup> do not agree well with the other datasets. Furthermore, there is no data for vapor pressures at temperatures below 250 K. Most of the vapor pressure data are located in a narrow temperature region between 280 K and 345 K, with deviations mostly within  $\pm 0.4$  %. At temperatures higher than 345 K, the deviations of data from Crowder *et al.*<sup>25</sup> are generally within  $\pm 2$  %. The AADs in saturated liquid density are Cochran et al.,<sup>42</sup> 1.0 %, Dias et al.,<sup>58</sup> 0.038 %, Dunlap et al.,<sup>32</sup> 0.29 %, Ermakov and Skripov,<sup>30</sup> 1.0 %, Hallewell et al.,<sup>51</sup> 0.40 %, Kennan and Pollack,<sup>59</sup> 0.13 %, Stiles and Cady,<sup>34</sup> 0.46 %, and Taylor et al.,<sup>39</sup> 4.1 %, respectively. Figure 10 shows that most of the datasets are located at temperatures between 265 K and 325 K, but they are contrary to each other. The datasets of Dias et al.<sup>58</sup> and Kennan and Pollack<sup>59</sup> can be fitted to agree well with the equation of state of this work. The deviations of most of their data are within  $\pm 0.15$  %. The AADs in saturated vapor density for the datasets of Ermakov and Skripov<sup>30</sup> and Taylor *et al.*<sup>39</sup> are 6.9 % and 20 %, respectively. Figure 11 illustrates that the saturated vapor density data are very sparse, and not accurate enough to determine the uncertainty in saturated vapor density of the equation of state, which also yields for the other two fluids.



Figure 9. Comparisons of vapor pressures calculated with the equation of state for n-perfluorohexane to experimental data.



Figure 10. Comparisons of saturated liquid densities calculated with the equation of state for *n*-perfluorohexane to experimental data.



Figure 11. Comparisons of saturated vapor densities calculated with the equation of state for *n*-perfluorohexane to experimental data.

#### 5.2. $p\rho T$ data and virial coefficients

# 5.2.1. *n*-perfluorobutane

Figure 12 compares densities calculated with the equation of state for *n*-perfluorobutane to experimental data and molecular simulation data of this work. In the liquid phase, only saturated liquid data are available, and were discussed in the previous section 5.1.1. In the vapor phase, there is only one experimental  $p\rho T$  dataset reported by Brown and Mears<sup>7</sup> and covering a narrow temperature range between 338 K and 455 K, with pressures up to 5.4 MPa. As shown in Table 11, the absolute average deviation is 1.1 %, and the absolute average deviation of the molecular simulation data is 2.8 %. The uncertainty in density of the equation of state for *n*-perfluorobutane is 1.0 % in the vapor phase region at temperatures between 338 K and 455 K. The molecular simulation data deviate by up to 5.5 % at very high temperature and pressure. Since there are no experimental data available to compare with, no statement on uncertainty of calculating densities can be made in this region. Figure 13 exhibits comparisons of the second virial coefficients calculated with the equation of state for *n*-perfluorobutane to experimental data. Five points were reported by Dantzler and Knobler<sup>53</sup> and Tripp and Dunlap.<sup>54</sup> Additionally some molecular simulation data from Köster *et al*<sup>18</sup> are available. However, they do not agree well with each other.

The AADs in the second virial coefficients of Dantzler and Knobler,<sup>53</sup> Tripp and Dunlap,<sup>54</sup> and Köster *et al.* (simulation data)<sup>18</sup> are 37 cm<sup>3</sup>·mol<sup>-1</sup>, 96 cm<sup>3</sup>·mol<sup>-1</sup>, and 14 cm<sup>3</sup>·mol<sup>-1</sup>, respectively.



Figure 12. Comparisons of densities calculated with the equation of state for *n*-perfluorobutane to experimental and simulated data of this work.



Figure 13. Comparisons of second virial coefficients calculated with the equation of state for *n*-perfluorobutane to experimental and simulated data.

# 5.2.2. *n*-perfluoropentane

Figure 14 compares densities calculated with the equation of state for *n*-perfluoropentane to experimental data. There is only one  $p\rho T$  dataset, from Aftienjew and Zawisza,<sup>28</sup> which extends

over a temperature range between 333 K and 504 K, with pressures up to 4.5 MPa. As shown in Table 12, the absolute average deviation is 0.77 %. Most of the  $p\rho T$  experimental data deviate by less than 0.9 %. Therefore, the uncertainty in density of the equation of state for *n*-perfluoropentane is estimated to be 0.9 % at temperatures between 330 K and 500 K. Figure 15 exhibits comparisons of the second virial coefficients calculated with the equation of state for *n*-perfluoropentane to experimental data. The reported data of Dantzler and Knobler<sup>53</sup> and Garner and McCoubrey<sup>56</sup> are 42 cm<sup>3</sup>·mol<sup>-1</sup> and 31 cm<sup>3</sup>·mol<sup>-1</sup>, respectively.



Figure 14. Comparisons of densities calculated with the equation of state for *n*-perfluoropentane to experimental data.



Figure 15. Comparisons of second virial coefficients calculated with the equation of state for *n*-perfluoropentane to experimental data.

# 5.2.3. *n*-perfluorohexane

Figure 16 compares densities calculated with the equation of state for *n*-perfluorohexane to

experimental data. There are three  $p\rho T$  datasets from Dunlap *et al.*,<sup>32</sup> 0.45 %, Piñeiro *et al.*,<sup>60</sup> 0.045 %, and Strejc *et al.*,<sup>61</sup> 0.45 %. The datasets of Dunlap *et al.*<sup>32</sup> and Strejc *et al.*<sup>61</sup> consist of only a few data points at a pressure of 0.1 MPa, and do not agree well with the dataset of Piñeiro *et al.*<sup>60</sup> Figure 16 shows that the deviations of most  $p\rho T$  experimental data are located within  $\pm 0.15$  %, so the uncertainty in density of the equation of state for *n*-perfluorohexane is estimated to be 0.2 % at temperatures between 280 K and 315 K. Figures 17 and 18 exhibit comparisons of the second virial coefficients and third virial coefficients calculated with the equation of state for *n*-perfluorohexane to experimental data. The reported data for the second virial coefficients are very scattered, and there is only one dataset for the third virial coefficients. As shown in Table 13, the AADs in the second virial coefficients of Dantzler and Knobler,<sup>53</sup> Garner and McCoubrey,<sup>56</sup> and Taylor *et al.*<sup>39</sup> are 45 cm<sup>3</sup>·mol<sup>-1</sup>, 55 cm<sup>3</sup>·mol<sup>-1</sup>, and 19 cm<sup>3</sup>·mol<sup>-1</sup>, respectively, and in the third virial coefficients of Taylor *et al.*<sup>39</sup> is 58 cm<sup>6</sup>·mol<sup>-2</sup>.



Figure 16. Comparisons of densities calculated with the equation of state for *n*-perfluorohexane to experimental data.



**Figure 17.** Comparisons of second virial coefficients calculated with the equation of state for *n*-perfluorohexane to experimental data.



Figure 18. Comparisons of third virial coefficients calculated with the equation of state for *n*-perfluorohexane to experimental data.

# 5.2.4. Behavior of thermal virial coefficients

Figure 19 displays calculations of  $(Z-1)/\rho$  from the equation of state of *n*-perfluorobutane along isotherms versus density  $\rho$  in the vapor-phase region. In this plot, the *y* intercept (zero density) represents the second virial coefficient at the given temperature, and the slope of each line at zero density represents the third virial coefficient. Therefore, this plot can give a sign if the behavior of the second and third virial coefficients of the equation is not reasonable. From Figure 19, the isotherms are straight in the vapor phase region and do not cross, thus, showing reasonable behavior. Figure 20 displays the shapes of *B*, *C*, and *D* (thermal virial coefficients) from the equation of state for *n*-perfluoropentane versus temperature. Each of these should go to negative infinity at zero temperature, pass though zero at a moderate temperature, increase to a maximum, and then approach zero at extremely high temperatures.<sup>40, 63, 64</sup> For the fourth virial coefficient, there should be a second maximum that is less than the magnitude of the first maximum.<sup>63, 64</sup> At higher temperatures beyond the temperatures with zero virial coefficients, the *B*, *C*, and *D* virial coefficients should always be positive. The temperatures of the maximum of *C* and the first maximum of *D* should be near the critical temperature, but the temperature of the maximum of *B* should be much higher than the critical temperature. From Figure 20, the behavior of *B*, *C*, and  $D^{64}$  of the equations of state in this work are reasonable from low temperatures up to extremely high temperatures.



**Figure 19.** Calculations of  $(Z-1)/\rho$  from the equation of state for *n*-perfluorobutane along isotherms versus density  $\rho$  in the vapor-phase region. Isotherms are drawn between 200 K and 700 K in intervals of 25 K.



**Figure 20.** The second, third, and fourth thermal virial coefficients, *B*, *C*, and *D*, from the equation of state for *n*-perfluoropentane versus temperature. In this plot, the values along the y-axis are equal to the value of *B*, the value of  $10 \cdot C$  ( $C^*$ ), and the value of  $10 \cdot D$  ( $D^*$ ). The units of the virial coefficients are dm<sup>3</sup>·mol<sup>-1</sup>, dm<sup>6</sup>·mol<sup>-2</sup>, and dm<sup>9</sup>·mol<sup>-3</sup>, respectively.

# 5.3. Caloric data

#### 5.3.1. *n*-perfluorobutane

Figures 21 to 23 exhibit comparisons of speed of sound, isobaric heat capacities, and isochoric heat capacities calculated from the equation of state for *n*-perfluorobutane to experimental data and molecular simulation data of this work. For speed of sound, there are two experimental datasets from Vacek *et al.*<sup>52</sup> and Hallewell *et al.*<sup>51</sup> For isobaric and isochoric heat capacities, there is no experimental data, but the molecular simulation data from this work are available. As shown in Table 11, the AADs in speed of sound of Hallewell *et al.*,<sup>51</sup> the molecular simulation data of this work, and Vacek *et al.*<sup>52</sup> are 0.18 %, 8.2 %, and 0.42 %, respectively. For the molecular simulation data, the absolute deviations are less than 0.70 % at pressure lower than 1 MPa. In Figure 21, the pressures of those molecular simulation data are upper to 680 MPa, and their deviations increased with pressure increasing. So the molecular simulation data with pressure above 50 MPa are not recommended to use. The absolute average deviation in isobaric heat capacity of the molecular simulation data is 0.70 %. From Figure 21, the uncertainty in speed of sound of the equation of state for *n*-perfluorobutane is 0.4 % at temperatures between 255 K and 303 K.



Figure 21. Comparisons of speed of sound calculated with the equation of state for *n*-perfluorobutane to experimental and simulated data of this work.



Figure 22. Comparisons of isobaric heat capacities calculated with the equation of state for *n*-perfluorobutane to simulated data of this work.



Figure 23. Comparisons of isochoric heat capacities calculated with the equation of state for n-

perfluorobutane to simulated data of this work.

# 5.3.2. *n*-perfluoropentane

Figures 24 and 25 exhibit comparisons of speed of sound and isobaric heat capacities calculated with the equation of state for *n*-perfluoropentane to experimental data. For both these properties, there is only one experimental dataset from Cochran *et al.*,<sup>42</sup> with a purity of 90.9 % for *n*-perfluoropentane.



Figure 24. Comparisons of speed of sound calculated with the equation of state for n-perfluoropentane to experimental data.



Figure 25. Comparisons of isobaric heat capacities calculated with the equation of state for n-perfluoropentane to experimental data.

# 5.3.3. *n*-perfluorohexane

Figures 26 and 27 show comparisons of speed of sound and isobaric heat capacities calculated with the equation of state for *n*-perfluorohexane to experimental data. Cochran *et al.*<sup>42</sup> also published speed of sound and isobaric heat capacity data for *n*-perfluorohexane. However, the data

from Cochran *et al.*<sup>42</sup> for *n*-perfluoropentane and *n*-perfluorohexane do not differ by much at the same temperature. Another dataset from Hallewell *et al.*<sup>51</sup> also reported speed of sound data. But this dataset does not agree well with the dataset from Cochran *et al.*<sup>42</sup> Therefore, the data from Cochran *et al.*<sup>42</sup> may have higher uncertainties than that reported in their paper, most likely due to the purity. From Table 13, the absolute average deviation in speed of sound of Hallewell *et al.*<sup>51</sup> is 0.61 %. The uncertainty in speed of sound of the equation of state for *n*-perfluorohexane is 1.0 % at temperatures between 278 K and 298 K.



Figure 26. Comparisons of speed of sound calculated with the equation of state for n-perfluorohexane to experimental data.





# 5.4. Extrapolation behavior

In addition to comparisons between calculated values from an equation of state and experimental data, the extrapolation behavior of thermodynamic properties is also crucial to assess the quality

of equations of state.

Figures 28 and 29 display isochoric heat capacity calculated from the equation of state for *n*-perfluorohexane and isobaric heat capacity for *n*-perfluorobutane versus temperature along isobars at pressures from zero to high values. For all fluids, the isochoric heat capacity and the isobaric heat capacity should reach a local maximum at the critical-point along the saturation line, and the curvature should be positive. Both figures show that the equations of state of this work behave appropriately within the range of validity, even at higher temperatures and pressures.



**Figure 28.** Isochoric heat capacities  $c_v$  calculated from the equation of state for *n*-perfluorohexane versus temperature along isobars. Isobars are shown at pressures of 0, 0.1, 0.5, 1,  $p_c$ , 4, 6, 8, 10, 20, 50, 100, 200, 500, and 10 000 MPa.



**Figure 29.** Isobaric heat capacities  $c_p$  calculated from the equation of state for *n*-perfluorobutane versus temperature along isobars. Isobars are shown at pressures of 0, 0.5, 1,  $p_c$ , 4, 6, 8, 10, 50, 100, 500, 1000, 2000, 5000, 10 000, 50 000, and 100 000 MPa.

Figure 30 shows speed of sound calculated from the equation of state for *n*-perfluoropentane versus temperature along the saturation lines and isobars at pressures from zero to 5000 MPa. Near the critical temperature, the slope and curvature of the saturated liquid and vapor speed of sound

with respect to temperature should be negative. This figure shows that the liquid saturation line has negative slope and is smooth even at very low temperatures (near 0 K), and the isobars even at very high pressures are smooth and do not cross. The equations for the other two fluids are very similar. Therefore, the equations of state of this work have reasonable extrapolation behavior at extremely low and high temperatures, and at high pressures.



**Figure 30.** Speed of sound *w* calculated from the equation of state for *n*-perfluoropentane versus temperature along isobars. Isobars are shown at pressures of 0, 0.5, 1,  $p_c$ , 4, 6, 8, 10, 20, 50, 100, 200, 500, 1000, 2000, and 5000 MPa.

Figures 31 and 32 demonstrate the density behavior along isobars calculated from the equation of state for *n*-perfluorohexane and isotherms calculated from the equation of state for *n*perfluorobutane, respectively. As shown in these figures, the isobars and isotherms are very smooth and do not cross within the region of validity, as well as at extremely high temperatures and pressures. The reasonable behavior at high temperatures and pressures comes from the term with  $t_i = 1$  and  $d_i = 4$ , as explained in Lemmon and Jacobsen,<sup>40</sup> and the fifth polynomial term with  $d_i = 3$ , as discussed in section 4.3 of this work.



**Figure 31.** Temperature versus density along isobars calculated from the equation of state for *n*-perfluorohexane. Isobars are shown at pressures of 0.1, 0.2, 0.5, 1,  $p_c$ , 4, 6, 8, 10, 20, 50, 100, 200, 500, and 1000 MPa.



**Figure 32.** Pressure versus density at extreme conditions of temperature and pressure along isotherms calculated from the equation of state for *n*-perfluorobutane. Isotherms are shown at temperatures of  $T_{\rm tp}$ ,  $T_{\rm c}$ ,  $10^3$ ,  $10^4$ ,  $10^5$ ,  $10^6$ ,  $10^7$ ,  $10^8$ , and  $10^9$  K.

The phase identification parameter (PIP)<sup>65</sup>  $\Pi$  is a property that can be used to differentiate the vapor phase from the liquid phase. States in the liquid phase have a value greater than 1, and states in the vapor phase have a value less than 1. It is defined as

$$\Pi = 2 - \rho \left[ \left( \frac{\partial^2 p}{\partial \rho \partial T} \right) \middle/ \left( \frac{\partial p}{\partial T} \right)_{\rho} - \left( \frac{\partial^2 p}{\partial \rho^2} \right)_T \middle/ \left( \frac{\partial p}{\partial \rho} \right)_T \right].$$
(13)

Figure 33 shows the phase identification parameter calculated from the equation of state for nperfluoropentane versus temperature along isobars between 0.1 MPa and 2000 MPa. In this plot, the phase identification parameter increases with increasing temperature, and reaches very high positive values at the critical temperature along the liquid saturation line. It shows opposite behavior along the vapor saturation line as compared to the liquid saturation line. Figure 34 displays the phase identification parameter calculated from the equation of state for *n*perfluorohexane versus density along isotherms below 5000 K. As shown in this figure, the phase identification parameter decreases with increasing density along the liquid and vapor saturation line. With increasing density, its value along isotherms reduces first, then starts to increase at a density near but below the critical density, then reduces again at densities greater than the critical density, with decreasing curvature as the density increases.



**Figure 33.** Phase identification parameter versus temperature along isobars calculated from the equation of state for *n*-perfluoropentane. Isobars are shown at pressures of 0.1, 0.2, 0.5, 1,  $p_c$ , 5, 10, 15, 20, 25, 30, 35, 50, 100, 200, 500, 1000 and 2000 MPa.



**Figure 34.** Phase identification parameter versus density along isotherms calculated from the equation of state for *n*-perfluorohexane. Isotherms are shown at temperatures of 150, 200, 250, 300, 350, 400,  $T_c$ , 450, 500, 600, 800, 1000, 1200, 1500, 2000, 3000, and 5000 K.

The Grüneisen parameter  $\Gamma$  is also a very sensitive property that helps to identify wrong

behavior of an equation of state. It is defined as

$$\Gamma = \left(\frac{\partial p}{\partial T}\right)_{\rho} / (c_{\nu}\rho).$$
(14)

Figure 35 shows the Grüneisen parameter of the equation of state for *n*-perfluorobutane versus density along isotherms between 100 K and 5000 K. The slope of the Grüneisen parameter with respect to density along isotherms is positive in the liquid phase, and the curvature is negative at high densities. Figure 36 shows the Grüneisen parameter calculated from the equation of state for *n*-perfluoropentane versus the logarithm of temperature along isochores between 0 and 100 mol·dm<sup>-3</sup>. The Grüneisen parameter at low temperatures for high density isochores shows low curvature as it approaches 0 K. As shown in Figure 36, the curvature of the Grüneisen parameter with respect to the logarithm of temperature along the liquid saturation line and along isochores changes from negative to positive with increasing temperature. This change happens at temperatures near and below the triple-point temperature, because the ideal heat capacity equation, exhibited by the isochore at 0 mol·dm<sup>-3</sup> shown in Figure 29, changes its curvature at a similar temperature.



**Figure 35.** Grüneisen parameter versus density along isotherms calculated from the equation of state for *n*-perfluorobutane. Isotherms are shown at temperatures of 100, 200, 300, 400, 500, 700, 1000, 1500, 2000, 2500, 3000, 4000, and 5000 K.



**Figure 36.** Grüneisen parameter versus the logarithm of temperature along isochores calculated from the equation of state for *n*-perfluoropentane. Isochores are shown between zero and 22 mol·dm<sup>-3</sup> in intervals of 2 mol·dm<sup>-3</sup>, and at densities of 0.5, 1, 25, 30, 40, 50, and 100 mol·dm<sup>-3</sup>.

As discussed in section 4.3, the third and fourth polynomial terms in Equation 10 are critical to the behavior of the isochoric and isobaric heat capacities in the liquid phase at low temperatures. When both of the temperature exponents in the third  $(d_i = 1)$  and fourth  $(d_i = 2)$  polynomial terms are larger than 1, but near 1, at low temperatures far from the triple-point temperature the rapid increase of the heat capacities towards infinity with temperature approaching 0 K becomes less. Likewise, the PIP increases as temperature decreases, and the Grüneisen parameter decreases with decreasing temperature along the saturation line and along isochores. When each of the temperature exponents of the third  $(d_i = 1)$  and fourth  $(d_i = 2)$  polynomial terms is smaller than 1, but near 1, at low temperatures far from the triple-point temperature the heat capacities decrease with temperature decreasing and, when approaching 0 K along isochores, the PIP decreases and the Grüneisen parameter rapidly increases toward infinity with temperature decreasing along the saturation line and along isochores. Additionally, calculated values of the Grüneisen parameter cross along isochores. When the temperature exponent of the fourth polynomial term  $(d_i=2)$  is smaller than 1, but near 1, the heat capacities go to negative infinity as the temperature decreases towards 0 K. Therefore, we chose an exact value of one for the temperature exponents of the third  $(d_i = 1)$  and fourth  $(d_i = 2)$  polynomial terms in Equation 10.

Figure 37 displays the characteristic (ideal) curves of the equation of state for *n*-perfluorohexane as a function of reduced temperature  $T/T_c$  and reduced pressure  $p/p_c$ . These ideal curves help to assess the behavior of an equation of state at high temperatures and pressures not covered by experimental data.<sup>66</sup> The ideal curves include the Boyle curve, the Joule-Thomson inversion curve, the Joule inversion curve, and the ideal curve, and they describe the behavior of the compressibility factor  $Z=p/\rho RT$  or its derivatives. As shown in Figure 37, these characteristic curves are smooth, indicating that the equations of state of this work have reasonable extrapolation behavior at high temperatures and pressures not covered by experimental data.



**Figure 37.** Characteristic (ideal) curves of the equation of state for *n*-perfluorohexane as a function of reduced temperature  $T/T_c$  and reduced pressure  $p/p_c$ .

# **6.** Conclusions

Helmholtz energy equations of state for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane were developed based on saturated properties,  $p\rho T$  data, caloric properties, and molecular simulation data. Ancillary equations for vapor pressure and saturated densities of these three fluids have been developed and can be used for fast approximation to calculate the saturated properties and to provide initial values in an iterative method to obtain the saturated states from the equations of state. The equations of state have reasonable behavior both within and outside the region of validity, and can be extrapolated even to extremely high temperatures and pressures, and to low temperatures.

The equation of state for *n*-perfluorobutane is valid from 144.0 K (the triple point temperature) to 450 K, with pressures up to 10 MPa and densities up to 8.61 mol·dm<sup>-3</sup>, which is the saturated liquid density at the triple point temperature. The uncertainty (k=2, indicating a level of confidence of 95 %) of the equation of state in density is 1.0 % in the vapor phase region at temperatures between 338 K and 455 K. The uncertainty in vapor pressure of the equation of state is generally less than 0.2 % at temperatures between 260 K and 380 K. The uncertainty in saturated-liquid density and at atmospheric pressure is generally less than 0.2 % between 230 K and 360 K. The uncertainty in saturated-vapor density is generally less than 2.0 % between 230 K and 360 K. The uncertainty in speed of sound is 0.4 % at temperatures between 255 K and 303 K. The uncertainties above atmospheric pressure are unknown due to the lack of data.

The equation of state for *n*-perfluoropentane is valid from 148.21 K (the triple point temperature) to 500 K, with pressures up to 10 MPa and densities up to 7.12 mol·dm<sup>-3</sup>. The uncertainty of the equation of state in density is 0.9 % at temperatures between 333 K and 504 K. The uncertainty in vapor pressure is generally less than 0.1 % between 220 K and 410 K. The uncertainty in saturated-liquid density and at atmospheric pressure is 0.3 % between 180 K and 410 K. The uncertainty in saturated-vapor density is estimated to be 2.0 % between 330 K and 410 K.

The equation of state for *n*-perfluorohexane is valid from 187.07 K (the triple point temperature) to 450 K, with pressures up to 40 MPa and densities up to 5.89 mol·dm<sup>-3</sup>. The uncertainty of the equation of state in density is 0.2 % at temperatures between 283 K and 313 K. The uncertainty in vapor pressure is generally less than 0.2 % between 280 K and 345 K. The uncertainty in saturated-liquid density is 0.15 % between 275 K and 315 K. The uncertainty in speed of sound is estimated to be 1.0 % at temperatures between 278 K and 298 K at atmospheric pressure.

Calculated values of properties in the liquid, vapor, and supercritical regions from the equations

of state for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane are given in Table 14 with the latest molar gas constant,  $R = 8.314462618 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , used in REFPROP 10.1 and can be used to validate computer code. The state points at zero density can be used to test the ideal-gas properties. The states close to the critical point are given for testing states where the properties of the fluids change rapidly. With the molar gas constant, R = 8.3144598 J·mol<sup>-1</sup>·K<sup>-1</sup>, used in REFPROP 10.0,<sup>67</sup> the values calculated from REFPROP 10.0 should be slightly different form Table 14.

Table 14. Calcu	<b>Fable 14.</b> Calculated values of properties from the equations of state with the latest molar gas constant value										
Temperature	Density	Pressure	Isochoric Heat	Isobaric Heat	Speed of Sound	Enthalpy	Entropy				
Т	ρ	р	Capacity $c_v$	Capacity $c_p$	w	h	S				
K	mol·dm <sup>-3</sup>	MPa	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	$\mathbf{m} \cdot \mathbf{s}^{-1}$	kJ∙mol <sup>–1</sup>	$J \cdot mol^{-1} \cdot K^{-1}$				
			<i>n</i> -Perflu	iorobutane							
225.0	0.0	0.0	171.2260	179.5405	90.78029	14.88551	Infinite				
225.0	7.8	37.55722	192.9387	246.5760	758.5512	-8.747458	-55.99954				
360.0	5.2	3.128110	223.0894	303.2828	226.8389	24.85197	77.45943				
387.0	2.637	2.355390	236.7771	8976.589	49.32548	37.43821	111.3057				
380.0	0.35	0.9312025	218.1084	236.8580	99.66618	44.83037	135.8261				
400.0	3.6	3.513083	233.3552	437.7846	89.44035	38.40444	112.8369				
			<i>n</i> -Perflu	oropentane							
250.0	0.0	0.0	199.2576	207.5721	86.70462	15.00556	Infinite				
250.0	6.5	45.74829	219.3241	268.4391	769.7973	-10.43608	-64.99865				
390.0	4.2	1.496384	273.9917	375.3160	182.6921	29.10127	83.36270				
421.5	2.17	2.083314	302.6768	15207.46	41.76442	44.91926	121.6715				
410.0	0.3	0.841555	273.0757	294.6374	91.41883	51.90776	143.3826				
450.0	3.0	4.159190	297.3112	431.0872	99.09973	51.36937	134.6778				
	<i>n</i> -Perfluorohexane										
260.0	0.0	0.0	244.6528	252.9673	81.31590	9.955560	Infinite				
260.0	5.5	28.03371	270.3971	329.6023	730.8597	-21.42844	-91.21752				
410.0	3.7	0.9573522	336.7461	435.6546	181.2565	31.64675	85.06658				
448.5	1.825	1.758863	363.5137	16301.72	36.59010	53.05034	133.9994				
430.0	0.23	0.6728015	330.4599	352.0829	85.33926	58.08506	150.4846				
460.0	2.7	2.671262	358.0500	541.4677	81.00252	53.96219	135.1519				

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# **Supporting Information**

In the supplementary material, fluid files for application in the software packages REFPROP<sup>67</sup> and

TREND<sup>68</sup> are provided (C4F10.FLD, C5F12.FLD, and C6F14.FLD). Furthermore, a stand-alone

Python script is available for the calculation of common thermodynamic properties with the present equations of state for *n*-perfluorobutane, *n*-perfluoropentane, and *n*-perfluorohexane (PFC.py). Additional Python files for use in CoolProp<sup>69</sup> are also provided (C4F10.json, C5F12.json, C6F14.json, and test CoolProp PFC.py).

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