

## Predicting the Surface Tension of Refrigerants from Density Gradient Theory and Perturbed Hard-sphere Equation of State

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(Received 2 May 2021, Accepted 10 July 2021)

The surface tensions of pure refrigerants were predicted using a density gradient theory (DGT) coupled with a perturbed hard-sphere equation of state (EoS) approach. The EoS is taken from the Carnahan-Starling hard-sphere equation with the perturbation term of Dohm-Prausnitz (CS-DP EoS), in which the relevant parameters to the molecular size and energies are universal functions of temperature in describing the equilibrium bulk properties. Then DGT+CS-DP EoS model has been employed for predicting the surface tension of 26 pure refrigerants taken from a Chemistry Webbook provided by NIST. Our calculations on the surface tension data from the DGT+CS-DP model led to an average absolute deviation of 4.84%. Then, the degree of accuracy of DGT+CS-DP model has also been compared with another DGT-based model.

Nomenclature and Units	
AAD	Average absolute relative deviation
$\gamma$	Surface tension ( $\text{mN m}^{-1}$ )
$T$	Absolute temperature (K)
$\rho$	Molar density ( $\text{mol m}^{-3}$ )
$y$	Packing fraction
$k_B$	Boltzmann constant ( $\text{J K}^{-1}$ )
$\mu$	Chemical potential
$a(\rho)$	Free energy density
$A$	Helmholtz free energy
$P$	pressure (Pa)
$\omega$	Grand free energy density
$c$	Influence parameters
$a_1$ - $b_3$	Fit coefficients to be used in characteristic functions, $F_a$ and $F_b$
$W$	Acentric factor
Superscripts	
HS	Hard-sphere repulsion
Exp	Experimental data
NIST	NIST databank
Calc.	Calculated values
Corr.	Correlated values
Subscripts	
s	Saturated state

**Keywords:** Surface tension, Refrigerant, Density gradient theory, Equation of state

## INTRODUCTION

The air-liquid interfacial tension (or that of surface tension) is an important property in the study of physics and chemistry at free surfaces. It affects the transfer rates of vapor absorption where a vapor-liquid interface exists. Such data are of importance to scientists and engineers. Pure refrigerants and refrigerant mixtures are widely used as working fluids in industrial applications involving refrigerators and heat pumps. Then the knowledge of the thermo-physical properties of refrigerant fluids especially their vapor-liquid equilibrium (VLE) behavior and air-liquid interfacial tension (or that of surface tension) is of importance as those properties affect the nucleation of bubbles in evaporators and the drainage of condensation from condenser surfaces [1-3]. Such knowledge is also fruitful to take a theoretical insight on the intermolecular forces operating in refrigerant mixtures systems. The refrigerants which are going to be investigated here belong to the hydrofluorocarbons (HFCs) category. Generally, HFCs have been used as acceptable alternatives to chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) because they contain no chlorine and thus they are harmless to the ozone layer, that is why they have come into focus in both the scientific community and refrigeration industries [4-8]. In view of the hazardous aspect of refrigerants for the atmosphere, the direct measurement of their VLE behavior over a wide range of temperatures is somewhat impractical. In this regard, the development of predictive methods for the air-liquid interfacial properties of refrigerant fluids can be highly useful.

Numerous studies have yet been carried out to correlate and predict the surface tensions of refrigerant fluids based on the various approaches such as the empirical approaches [9-14], computer-aided methods [15-16], and those are based on semi-theoretical models.

Among the empirical approaches, Cachadiña *et al.* [9-11] and Tian *et al.* [17] made fruitful efforts to correlate the surface tensions of a wide variety of refrigerants using several simple equations. Also, Li *et al.* [18] predicted the surface tension of 21 pure refrigerants by an improved

equation based on the principle of corresponding states with double referenced fluids. For instance, Cachadiña *et al.* [10] developed some simple equations to correlate the surface tension data of a wide variety of pure refrigerants. They obtained the AADs below 5% for 63 refrigerants of all 83 refrigerants considered, and only for 4 of them, the AADs were greater than 10%.

Among the computer-aided approaches, the ANN is the most widely used one for the prediction of surface tension of refrigerant fluids [15-16,19-20]. In 2019, Hosseini [21] estimated the surface tension of 8 pure refrigerants with the help of Escobedo-Mansoori parachor-based relation [22] with the AARD of 4.76%.

However, the most widely used semi-theoretical models are coming from the Fowler-Kirkwood-Buff (FKB) approximation [23-28] and the density gradient theory [29-30] with the equations of state through which the Helmholtz free energy density and the bulk properties are determined. FKB [23-24] approximation relates the bulk densities of vapor and liquid to the pair potential and distribution function at the vapor-liquid interface. Also, several efforts have yet been carried out to devolve some molecular thermodynamic models for the correlation of surface tension of a wide variety of fluids [26-28,31-36].

In the meanwhile, the development of density gradient theory-based approaches for the calculation of surface tension is growing rapidly in the context of semi-classical thermodynamics. So far, several authors have utilized the density gradient theory considerations for predicting the surface tension of a wide variety of fluids from pure non-polar and polar liquids [29,37-44].

The DGT-based models demand an equation of state for the calculation of Helmholtz free energy density as well as the chemical potential. The work aims to develop a combined density gradient theory with Dohm-Prausnitz, EoS model (let's call that as DGT+CS-DP) for the prediction of surface tensions of refrigerant fluids. The original scheme utilizes the universal parameters relevant to the molecular size and energies.

Consequently, to test the choice of the universal parameters of CS-DP EoS, and the capability of them to predict the surface tension of pure refrigerants, we compare the results from DGT+CD-DP EoS model with the NIST database [45].

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## DENSITY GRADIENT THEORY OF INTERFACE

Density functional theories start by expressing the Helmholtz free energy of the system,  $A$ , as a function of the density profile in which the Helmholtz free energy density can be expanded in terms of the bulk values [46-47]:

$$A[\rho(r)] = \int dr \left\{ a(\rho(r)) + \frac{C}{2[\nabla\rho(r)]^2} \right\} \quad (1)$$

where  $a(\rho(r))$  is the Helmholtz free energy density of the bulk phases,  $\rho(r)$  is the molecular density profile, and  $c$  is the influence parameter. For a planar interface, functional minimization of Eq. (1) for phase coexistence conditions leads to the following expression for the surface tension,  $\gamma$ :

$$\gamma = \int_{\rho_v}^{\rho_l} d\rho \sqrt{2c\Delta\omega(\rho)} \quad (2)$$

where, the integration takes place from the vapor bulk densities to the liquid one and  $\Delta\omega$ , the excess grand free energy density is given by:

$$\Delta\omega(\rho) = \alpha(\rho) - \mu\rho + P_s \quad (3)$$

where,  $P_s$  and  $\mu$  are the equilibrium pressure (or that of vapor-pressure) and chemical potential, respectively.

## EQUATION OF STATE CONSIDERATIONS

As mentioned earlier the DGT-based approaches demand some working EoS for the estimation of equilibrium bulk properties. In the present work, a perturbed hard-sphere (PHS) EoS is going to be employed for the estimation of equilibrium bulk properties including the saturated vapor and liquid densities, vapor-pressures as well as Helmholtz free energy, and the chemical potential of the refrigerants under study. For this purpose, we adopt an improved PHS EoS consisting of the Carnahan-Starling hard-sphere equation [48] with some simple perturbation terms proposed by Dohm-Prausnitz [49] to calculate the equilibrium bulk properties mentioned above. The PHS EoS under consideration can be read as:

$$Z^{CS-DP} = Z^{CS} + Z^{DP} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{4a}{RTb} \eta \Psi \quad (5)$$

where  $a$  is a molecular energy parameter reflecting intermolecular attractive forces and  $\eta$  is the packing fraction relating the bulk densities to the molecular size parameter,  $b$  via the following equation:

$$\eta = \frac{b\rho}{4} \quad (6)$$

The first term in the right hand of Eq. (4) represents the hard-sphere expression which is taken from Carnahan-Starling [48] and the second term is that of perturbation term of Dohm-Prausnitz [49]. They introduced a correction function into Eq. (5) (as indicated by  $\Psi$ ) for the fair representation of critical isotherms, that depends on the reduced packing fraction such that  $\Psi \rightarrow 1$  as  $\eta \rightarrow 0$ . Dohm-Prausnitz set up the  $a$  and  $b$  parameters for several simple fluids from argon to propene via the critical point criterial and the corresponding states correlations as follows:

$$a = 0.550408 \frac{R^2 T_c^2}{P_c} \times F_a(T_r) \quad (7)$$

$$b = 0.187276 \frac{RT_c}{P_c} \times F_b(T_r) \quad (8)$$

Where  $F_a$  and  $F_b$  are the universal functions of the reduced temperature,  $T_r (= T/T_c)$  as scaled by the critical temperature both of which can be reads as:

$$F_a(T_r) = a_1 \tan h \left( a_2 |T_r - 1|^{0.7} \right) + 1 \quad (9)$$

$$F_b(T_r) = b_1 \tan h \left( b_2 |\ln T_r|^{0.8} + 1 \right) \quad (10)$$

The coefficients  $a_1$ - $b_2$  are related to the acentric factor of pure fluid,  $w$  by:

$$a_1 = 0.367845 + 0.055966 w \quad (11)$$

$$a_2 = (-1)^m (0.604709 - 0.008477 w) \quad (12)$$

$$b_1 = 0.356983 + 0.190003 w \quad (13)$$

**Table 1.** The Critical Constants along with the Molecular Weights of Studied Refrigerants to be Used in CS-DP EoS. The Vales Taken from NIST Databank [45]

Refrigerant	M <sub>w</sub> (g mol <sup>-1</sup> )	T <sub>C</sub> (K)	P <sub>C</sub> (MPa)	w
Methane derivative				
R11	137.36	471.11	4.41	0.19
R12	120.9	385.12	4.14	0.18
R13	104.46	302.00	3.88	0.17
R14	88.01	227.51	3.75	0.18
R21	102.92	451.48	5.18	0.21
R22	86.5	369.29	4.99	0.22
R23	70.01	299.29	4.83	0.26
R32	52.02	351.25	5.78	0.28
Ethan derivative				
R113	187.4	487.21	3.40	0.25
R115	154.5	353.10	3.12	0.25
R116	138.01	293.03	3.05	0.26
R123	152.9	456.83	3.66	0.28
R124	136.5	395.42	3.62	0.29
R125	120.02	339.17	3.62	0.30
R134a	102.03	374.21	4.06	0.33
R141b	116.95	477.50	4.21	0.22
R142b	100.5	410.26	4.05	0.23
R143a	84.04	345.86	3.76	0.26
R152a	66.05	386.41	4.52	0.27
Propane derivative				
R218	188.02	345.02	2.64	0.32
R227ea	170.03	375.95	2.99	0.35
R236ea	152.04	412.44	3.50	0.38
R236fa	152.04	398.07	3.20	0.38
R245ca	134.05	447.57	3.92	0.35
R245fa	134.05	427.20	3.64	0.38
Cyclobutane derivative				
RC318	200.03	388.38	2.78	0.36

$$b_2 = (-1)^m (1.37 - 1.898981 w) \quad (14)$$

$$m = 0 \text{ for } T_r < 1 \text{ and } m = 1 \text{ for } T_r \geq 1$$

Now the equilibrium bulk properties of pure refrigerant can be estimated from CS-DP EoS with the universal

parameters (Eqs. (6)-(9)) and then surface tensions are calculated from the DGT+CS-DP model. The results are reported in the next section as the AAD of our calculations on the surface tensions from those reported in the NIST databank [45].

It should be added that the critical constants of studied

refrigerants along with their molecular weight to be used in both CS-DP and MCS-DP EoSs, were provided in Table 1.

## EQUILIBRIUM BULK PROPERTIES

To utilize the DGT+CS-DP model for the study of air-liquid interfacial tensions of refrigerants, we need to report the  $c$ -parameter values for all systems under study as their values were provided in Table 2. These values were obtained using the fitting of standard surface tension data of refrigerants reported by the NIST databank [45]. Now DGT+CS-DP model is ready to be utilized for calculating simultaneously the equilibrium bulk properties of refrigerants as well as their surface tension.

Firstly, the degree of accuracy of CS-DP EoS was assessed by calculating the equilibrium bulk properties of refrigerants including the saturated liquid densities and vapor-pressures. Our calculation results were summarized in Table 3 as the AAD of the calculations from the standard NIST databank [45]. As Table 3 shows the calculations were carried out for 26 pure refrigerants in 100-459 K range and vapor-pressures up to 3.15 MPa. As the results in Table 3 indicate, the CS-DP EoS shows the AAD of 4.05% for the saturated liquid densities and the AAD of 15.4% for vapor-pressures.

As mentioned above, we aimed to check the capability of the DGT+CS-DP model along with the  $c$ -parameter for calculating the surface tension data of studied systems as this property is required to analyze heat transfer problems [50]. The assessment of thermodynamic models using the surface tension is a somewhat routine approach that has already been performed by other researchers [26-28,31-36]. To utilize the DGT+CS-DP model for the study of surface tension of refrigerants, we need to report the  $c$ -parameter values for all systems as their values were provided in Table 2. These values were traditionally obtained using the fitting of several surface tension data.

Generally, the DGT+CS-DP model has been assessed by comparing the results with the surface tension data of NIST [45]. The results were reported in Table 4 as the AAD of correlated surface tension values from the NIST databank [45]. As it clears from Table 4, our calculations were carried out for 26 pure refrigerants of methane, ethane and propane, and cyclobutane derivatives in the 100-457 K range. From

**Table 2.** Influence Parameters,  $c$  of Studied Refrigerants to be Used in Eq. (2)

Refrigerant	$c \times 10^{19}$
R11	1.732
R12	1.125
R13	0.677
R14	0.345
R21	1.072
R22	0.598
R23	0.332
R32	0.251
R113	2.806
R115	1.383
R116	0.931
R123	1.760
R124	1.300
R125	0.870
R134a	0.752
R141b	1.722
R142b	1.110
R143a	0.708
R152a	0.567
R218	1.748
R227ea	1.706
R236ea	1.706
R236fa	1.499
R245ca	1.678
R245fa	1.570
Rc318	2.443

470 standard data points examined, the AAD of the DGT+CS-DP model was found to be 4.84% which reveals some acceptable accuracy in the current modeling once the universal parameters are used in CS-DP EoS. The predicted surface tension values of refrigerant systems studied along with the relative deviations from the NIST databank [45] were also provided in a supplementary data file (see Tables S1-S5) to this article.

To show graphically how the DGT+CS-DP model passes through the NIST data points, Fig. 1 has been provided as it comprises a relative deviation plot for the

**Table 3.** AAD<sup>a</sup> (in %) of Calculated Equilibrium Bulk Properties Including the  $\rho_s$  and  $P_s$  from CS-DP EoS, Compared with NIST Databank [45]

Refrigerant	$\Delta T$ (K)	$\Delta P$ (MPa)	NP <sup>b</sup>	AAD <sup>c</sup>	AAD <sup>f</sup>
R11	210-430	0.00-2.37	23	1.34	12.29
R12	173-353	0.00-2.29	19	1.62	12.18
R13	135-275	0.00-2.06	15	1.42	12.16
R14	100-210	0.00-2.19	12	3.08	12.43
R21	200-420	0.00-3.15	23	3.65	13.28
R22	165.73-335.73	0.00-2.57	17	4.11	13.05
R23	132-272	0.00-2.42	15	8.23	13.75
R32	185-325	0.01-3.28	15	15.97	14.70
R113	236.93-456.9	0.00-2.15	23	2.00	15.51
R115	173.76-333.76	0.00-2.10	17	2.47	14.43
R116	173.1-273.1	0.03-1.84	11	3.65	14.62
R123	205-435	0.00-2.57	24	3.11	16.43
R124	175-365	0.00-2.02	20	1.52	16.95
R125	175.52-312.52	0.00-1.98	15	1.60	16.68
R134a	169.85-349.85	0.00-2.45	19	4.81	17.36
R141b	210-440	0.00-2.38	24	3.26	13.95
R142b	180-380	0.00-2.36	21	4.60	13.76
R143a	161.34-311.34	0.00-1.75	16	9.01	14.47
R152a	180-350	0.00-2.19	18	10.11	14.79
R218	150-320	0.00-1.50	18	4.10	18.05
R227ea	205-345	0.01-1.55	15	4.44	16.79
R236ea	242-382	0.02-1.89	15	5.03	15.93
R236fa	180-360	0.00-1.46	19	1.97	21.02
R245ca	200-410	0.00-2.00	22	2.59	18.66
R245fa	200-390	0.00-1.80	20	1.90	20.41
Rc318	233.35-363.35	0.02-1.68	14	4.85	14.88
Overall			470	4.05	15.40

$$^a AAD = \frac{1}{100} \sum_{j=1}^n \frac{|X_S^{Calc.} - X_S^{NIST}|}{X_S^{NIST}}, x \text{ stands for an equilibrium property, i.e., saturated density and}$$

vapor pressures herein. <sup>b</sup>Number of data points examined. <sup>c</sup>AAD of saturated liquid density from original CS-DP EoS. <sup>f</sup>AAD of saturated vapor-pressure from original CS-DP EoS.

estimated surface tensions of the 8 typical refrigerants from the NIST databank. Let's give a discussion on the trend of relative deviations obtained from the DGT+CS-DP model when compared with the NIST databank. At the first glance, the results for 8 refrigerants show a systematic trend as the

$T_r$  increases, the relative deviations are approaching to zero, and then they are increasing toward the negative values as the reduced temperature rises even though for the case of R115, Rc318, and R32 the deviations approaching zero again at the temperatures near the  $Tr \approx 0.9$ .

**Table 4.** AAD (in %) <sup>a</sup> of the Calculated Surface Tensions of Studied Refrigerants Using the DGT+CS-DP Model from the Standard Data Reported by NIST [45]

Refrigerant	$\Delta T$ (K)	NP <sup>b</sup>	AAD <sup>d</sup>
R11	210-430	23	5.5935
R12	173-353	19	4.3403
R13	135-275	15	3.2806
R14	100-210	12	4.2338
R21	200-420	23	5.9609
R22	165.73-335.73	17	4.6265
R23	132-272	15	1.7025
R32	185-325	15	2.5534
R113	236.93-456.93	23	4.5319
R115	173.76-333.76	17	4.6919
R116	173.1-273.1	11	3.6699
R123	205-435	24	4.4279
R124	175-365	20	4.9912
R125	172.52-312.52	15	2.5085
R134a	169.85-349.85	19	2.3249
R141b	210-440	24	5.5819
R142b	180-380	21	5.7417
R143a	161.34-311.34	16	20.198
R152a	180-350	18	4.2728
R218	150-320	18	3.4417
R227ea	205-345	15	2.7338
R236ea	242-382	15	3.1914
R236fa	180-360	19	7.3039
R245ca	200-410	22	4.7891
R245fa	200-390	20	4.7423
Rc318	233.35-363.35	14	1.9602
Overall		470	4.84

$$^a AAD = \frac{100}{NP} \sum_{i=1}^n \left| \frac{\gamma^{Calc.} - \gamma^{NIST}}{\gamma^{NIST}} \right| \cdot ^b \text{Number of data points}$$

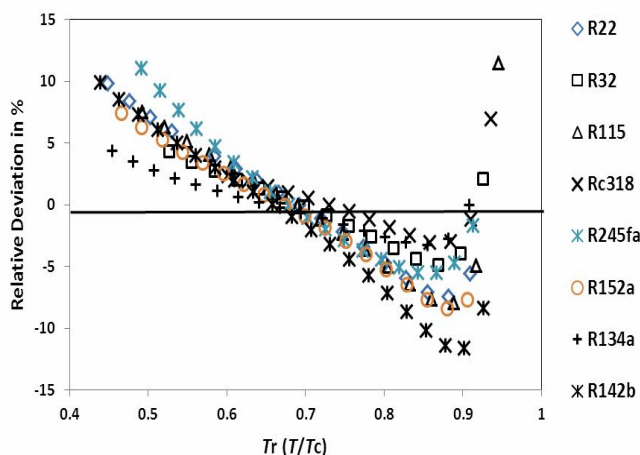
examined. <sup>d</sup> AAD of DGT+CS-DP model from NIST databank.

**Table 5.** AADs (in %) <sup>a</sup> of the Calculated Surface Tensions of Studied Refrigerants Using the DGT+CS-DP Model and those Obtained from the DGT+VTPR Model [30] from Standard Data Reported by NIST [45]

Refrigerant	$\Delta T$ (K)	NP <sup>b</sup>	AAD <sup>d</sup>	AAD <sup>c</sup>
R134a	169.85-349.85	19	2.32	1.78
R142b	180-380	21	5.74	2.63
R115	173.76-333.76	17	4.69	0.32
R32	185-325	15	2.55	2.19
R245fa	200-390	20	4.74	2.21
R227ea	205-345	15	2.73	6.57
R236fa	180-360	19	7.30	5.05
R113	236.93-456.93	23	4.53	3.06
R12	173-353	19	4.34	1.17
R124	175-365	20	4.99	1.98
Overall		180	4.48	2.65

$$^a AAD = \frac{100}{NP} \sum_{i=1}^n \left| \frac{\gamma^{Calc.} - \gamma^{NIST}}{\gamma^{NIST}} \right| \cdot ^b \text{Number of data points}$$

examined. <sup>d</sup> AAD of DGT+CS-DP model from NIST databank. <sup>c</sup> AAD of DGT+VTPR model from NIST databank.



**Fig. 1.** A relative deviation plot against the reduced temperature for the estimated surface tensions of several refrigerants studied using the DGT+CS-DP model from the NIST databank [45].

It would also be interesting to see how accurate the results from the DGT+CS-DP model when compared with another DGT-based approach such as the work of Lin *et al.* [30], who coupled the density gradient theory with a volume-translated Peng-Robinson (VTPR) EoS for the study of surface tension of pure non-polar and polar fluids including the refrigerants. Despite the present work, Lin *et al.* determined the influence parameters from a correlation that was generalized as a function of the critical compressibility factor, the acentric factor, the reduced dipole moment, and the reduced temperature. Our comparison results were summarized in Table 5 as the AAD of DGT+CS-DP model and DGT+VTPR model of Lin *et al.* from the NIST databank [45]. As Table 5 demonstrates, our comparison was carried out in 169.85-456.93 K range, from 180 data points examined, the AADs of calculated surface tensions from our DGT+CS-DP model and the DGT+VTPR [30] model of Lin *et al.* were found to be 4.48% and 2.65%, respectively, which reveals well the superiority of Lin *et al.* model against our model. The superiority of the DGT+VTPR model of Lin *et al.* is somewhat associated with several fit coefficients to be used in the correlation of influence parameter for each refrigerant which improved significantly the accuracy of calculations, even though the results are correlative rather than predictive.

## CONCLUSIONS

The tension at the surface of a liquid is one of the most striking demonstrations of the intermolecular forces. This work employed a semi-theoretical model based on the DGT for the correlation and prediction of surface tension of pure refrigerants, for which the values are taken from the standard databank, NIST.

The coupling of DGT coming from the molecular physics of interfacial tension with the EoS provided us a good opportunity to calculate simultaneously the equilibrium bulk properties as well as the surface tensions of refrigerants with good accuracies. Some critical analysis was also made to see how are the results obtained from the universal parameters to be used in the DGT+CS-DP model when compared with the data sources, NIST databank. This work also demonstrated that the proposed DGT+CS-DP model run out accurately for both equilibrium bulk

properties as well as the surface tensions calculations when the general parameters were used in the model development.

## ACKNOWLEDGMENTS

S.M. Hosseini is grateful to the University of Hormozgan for supporting the research.

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