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Temperature Dependence of Hamaker Constants for Fluorocarbon Compounds

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The effect of temperature on the liquid–vapor surface tension of fluorocarbon and hydrocarbon compounds starting from van der Waals interactions (calculated according to Lifshitz's theory) is studied. The correlation obtained is based on the reversibility of the process of separation of two liquid slabs, creating an intermediate vapor phase. The resulting surface tension can be expressed as a function of two surface potentials having simple dependences on temperature. Reasonable distances of closest approach between the slabs are obtained for all cases, including dispersion contributions between the molecules of water as a special case.

Introduction

Several theoretical models are available for the description of the variation of the surface tension as a function of temperature. Some of them start from Widom's scaling law and the law of correspondent states.¹ Empirical adjustments based on the critical temperature (T_C), the critical volume (V_C), and the acentric factor (ω) have been reported by Miqueu et al. to describe the variation of the tension with temperature for fluorocarbons and hydrocarbons.² Queimada et al.³ proposed a model of four parameters (T_C , V_C , Z_C , ω) for hydrocarbons including the compressibility factor Z_C . In both cases, however, the effect of temperature on the cohesive work remains unexplained, since these models do not take into account either surface forces or surface free energies in the description of the interaction between the liquid slabs.^{4–8} In the present paper, the variation of the surface tension with temperature is studied, introducing a temperature-dependent Hamaker constant and the concept of reversibility of the cohesive work.

Temperature Dependence of the Nonretarded Hamaker Constant for Identical Dielectric Slabs Separated by a Continuous Medium

Using pairwise additive van der Waals interactions between point molecules, Hamaker⁹ obtained a simple formula for the free energy of interaction (F) between two slabs interacting through a vacuum at a distance d :

$$F(d) = -\frac{A}{12\pi d^2} \quad (1)$$

where A is the Hamaker constant. This result was later reproduced by Grifalco and Good¹⁰ relating the free energies of cohesion of the interacting bodies to their free energy of adhesion.

The parametric dependence of the Hamaker constant requires a more elaborate theory which considers many-body interactions

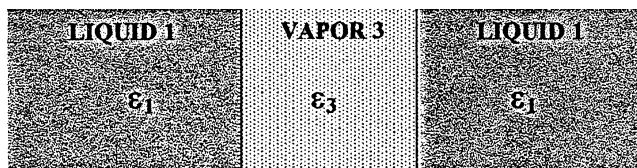


Figure 1. Parallel slabs of dielectric function ϵ_1 separated by a medium of permittivity ϵ_3 . We follow here the usual convention according to which a triad of subscripts (i, j, k) describes a system composed of two slabs of materials 1 ($i = 1$) and 2 ($k = 2$), separated by medium 3 ($j = 3$). In the case of two equal slabs, $i = 1 = k$, and $j = 3$.

and takes into account the separating medium.^{11–16} Figure 1 illustrates a system consisting of two slabs of material 1 interacting across medium 3. According to Lifshitz theory,¹¹ the fluctuating dipoles within these media establish electric fields that interact both constructively and destructively.⁶ As a result, only certain frequencies of electromagnetic radiation contribute to the dispersion interaction between the slabs. The resulting van der Waals interaction energy depends on the frequency-dependent dielectric spectra of the materials involved, and the geometry of the system. The nonretarded Hamaker function in the limit $d \rightarrow 0$ is given by a series expression:^{11–16}

$$A_{131} = \frac{3k_B T}{2} \sum_{n=0}^{\infty} \sum_{l=1}^{\infty} \frac{\Delta_{31}^{2l}}{l^3} \quad (2)$$

where T is the temperature, k_B the Boltzmann constant, A_{ijk} the Hamaker function between slabs i and k separated by medium j , and

$$\Delta_{31} = \frac{\epsilon_1(i\xi_n) - \epsilon_3(i\xi_n)}{\epsilon_1(i\xi_n) + \epsilon_3(i\xi_n)} \quad (3)$$

The frequencies ξ_n in eq 3 are equal to $n4\pi^2 k_B T/h$, where h is the Planck constant. $\epsilon_1(i\xi_n)$ and $\epsilon_3(i\xi_n)$ are real-valued functions with no direct physical meaning, corresponding to media 1 and 3, respectively. They can be determined from experiment through their relation to the complex dielectric

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function $\epsilon_m(\omega)$. The imaginary part of $\epsilon_m(\omega)$ depends on the absorption spectrum of material m at real frequency ω , and its real part is related to its index of refraction in regions of the spectrum where no absorption occurs.^{6,16}

The prime on the summation of eq 2 means that the “static” term $n = 0$ should be halved. This ($n = 0$) zero-frequency contribution includes Keesom and Debye dipolar contributions¹² and depends explicitly on T . The rest of the expression is frequency-dependent and includes the London energy contribution.¹²

Except for polar molecules with significant dipole relaxations in the microwave region of the spectrum, the major contribution to the Hamaker function (given by eq 2) comes from ultraviolet adsorption. The other terms are small and rarely contribute more than 5%.¹² This is the case of alkanes between 5 and 16 carbons as shown in ref 16.

Disregarding summation terms higher than $t > 1$ (in eq 2) and supposing similar frequencies $\omega_1 \approx \omega_3$ in the ultraviolet region ($\omega_{UV} \approx I/\hbar$), where I is the ionization potential, one obtains

$$A_{131} = \frac{3k_B T (\epsilon_1(0) - \epsilon_3(0))^2}{4 (\epsilon_1(0) + \epsilon_3(0))} + \frac{3\hbar\omega_{UV}}{32\pi\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \quad (4a)$$

where n_m stands for the index of refraction of material m and $\epsilon_m(0)$ corresponds to its static dielectric permittivity. This last equation also applies to the particular case where the interaction occurs between two liquid slabs of substance 1 in equilibrium with their vapor phase $j = 3$. Equation 4a is probably the most common expression for the calculation of the Hamaker constant A_{131} , although little knowledge is available concerning its temperature dependence.¹⁴

The limit of low temperatures ($T \rightarrow 0$) in the summation of eq 2 is equivalent to omitting the static term in the frequency summation. In this case only the implicit temperature dependence corresponding to $n \geq 1$ should be present. Under these conditions eq 4a can be simplified, obtaining

$$A_{131}(T \rightarrow 0) \approx \frac{3\hbar\omega_{UV}}{32\pi\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \quad (4b)$$

The above expression depends on temperature through the variation of the refractive indexes.

In this work we evaluate A_{131} at different temperatures for liquid–vapor systems in equilibrium. For this purpose we estimate the free energy of interaction (Lifshitz–van der Waals), F_{131}^{LW} , using the expression

$$F_{131}^{LW}(d, T) = \frac{A_{131}(d, T)}{12\pi d^2} \quad (5)$$

According to Grifalco and Good,¹⁰ an approximation of $A_{131}(T)$ may be obtained from $A_{131}(d, T)$ evaluated at the closest distance of approach between the slabs. This corresponds to the minimum value $d = l$ of the potential F_{131}^{LW} as a function of d :

$$F_{131}^{LW}(T) = \frac{A_{131}(T \rightarrow 0)}{12\pi l^2} + \left(\frac{\partial F_{131}^{LW}}{\partial T} \right) T \quad (6)$$

where the temperature dependence ($\partial F_{131}^{LW}/\partial T$) is a function of $\Delta_{13} (\xi_n = 0)$, i.e., of the difference of the static response between

the phases. The order of magnitude of the quantity ($\partial F_{131}^{LW}/\partial T$) can be obtained from eqs 6 and 4a. It corresponds to the static term of the Hamaker constant given by eq 4a divided by $12\pi l^2$. Considering typical values of the dielectric constant for the liquid hydrocarbons ($\epsilon_1(0) \approx 2$) and their vapor ($\epsilon_3(0) \approx 1$), along with an approximate van der Waals distance of approach of 2 Å, ($\partial F_{131}^{LW}/\partial T$) $\approx 7.6 \times 10^{-4}$ mJ/(m² K).

Reversibility of the Cohesive Work

In this paper the interaction between two liquid slabs is supposed to be the result of dispersion forces only, as formerly assumed by Hamaker in the deduction of eq 1. However, it is clear that orientation (o), induction (i), and coupling (c) effects¹⁵ should be taken into account for such an evaluation. Let us start from an expression of the cohesive work (W_{coh}), which includes all these contributions:

$$-W_{coh} = F_{disp}^{LW} + F_o + F_i + F_c \quad (7)$$

The reversibility of the process (reunification of the slabs) is guaranteed, making the cohesive work equal to the stored energy in the liquids once the two slabs are separated an infinite distance. Following the model of the interfacial tension previously developed in refs 17 and 18, we ascribe this energy per unit area (U_d) to an elastic deformation of the liquid network at the interface of each slab. Once the two slabs are well separated, this energy is equal to $-2\gamma_{13}$, where γ_{13} is the surface tension between the liquid (1) and vapor (3):

$$U_d = -2\gamma_{13} = -W_{coh} \quad (8)$$

Equivalently

$$U_d = F_{disp}^{LW} + F_o + F_i + F_c \quad (9)$$

This expression may be rewritten as

$$U_d = F_{disp}^{LW} + \phi_E \quad (10)$$

where the quantity ϕ_E is defined as a surface potential per unit area which includes all the nondispersive contributions to the interaction between the two slabs. Similarly, let us define the potential ϕ_L as

$$\phi_L = F_{disp}^{LW} + U_d \quad (11)$$

According to these definitions, the surface tension between the liquid slab (1) and the vapor (3) can be written as a function of these two potentials:

$$\gamma_{13} = -\frac{\phi_E + \phi_L}{4} \quad (12)$$

Notice that when $\phi_E = 0$, the above equation reduces to

$$\gamma_{13}(T) = -\frac{F_{131}^{LW}(T)}{2} = \frac{A_{131}^{LW}}{24\pi l^2} \quad (13)$$

This equation is commonly used to evaluate the interaction between nonpolar liquids, and through which the van der Waals typical distances l for hydrocarbons have been calculated.¹⁵

Following the definition of ϕ_L (eq 11) and the form of the dispersion interaction given by eq 6, the temperature dependence of ϕ_L is given by the following expression:

$$-\phi_L(T) = 2\gamma_{13}(T) + \frac{A_{131}(n_i^2(T))}{12\pi l^2} + \left(\frac{\partial F_{131}^{LW}}{\partial T}\right)_{\xi_n=0} T \quad (14)$$

We considered in this work the liquid–vapor systems for fluorocarbon coolers R124 (1-chloro-1,2,2,2-tetrafluoroethane), R236fa (1,1,1,3,3,3-hexafluoropropane), R236ea (1,1,1,2,3,3-hexafluoropropane), R245ca (1,1,2,2,3-pentafluoropropane), R245fa (1,1,1,3,3-pentafluoropropane), and E125 (pentafluorodimethyl ether), whose surface tensions and refraction indexes for liquid and vapor phases are reported by Schmidt et al.¹⁹ Since the value of A_{131} for each temperature can be calculated (see eq 4b), linear multivariable analysis can be used to analyze the variation of the surface tension of fluorocarbons as a function of T and l^{-2} (eq 14). From this analysis it is observed that ϕ_L appears to be always proportional to the temperature with a proportionality coefficient close to 0.30 mJ/(m² K) for all the systems studied. However, since $(\partial F_{131}^{LW}/\partial T)$ is on the order of 7.6×10^{-4} mJ/(m² K) as was previously estimated (only 0.25% of 0.30 mJ/(m² K)), the main temperature dependence of ϕ_L does not come from this contribution. If ϕ_L is supposed to be a well-behaved (continuous and differentiable) function of temperature, it can be expanded in series up to first order in T ($\phi_L = \phi_L^0 + (\partial\phi/\partial T)T$). Thus, the constant term of this potential is given by

$$-\phi_L^0(T) = 2\gamma_{13}(T) + \frac{A_{131}(n_i^2(T))}{12\pi l^2} + \left[\left(\frac{\partial F_{131}^{LW}}{\partial T}\right) + \left(\frac{\partial\phi_L}{\partial T}\right)\right]_{\xi_n=0} T \quad (15)$$

where ϕ_L^0 is the value of ϕ_L at $T \approx 0$. It may be expected that $(\partial\phi_L/\partial T)$ depends on Δ_{31} ($\xi_n = 0$), and on the difference between the static response of phases 1 and 3 of the system.

Figure 2 illustrates the potentials ϕ_L^0 and ϕ_E for fluorocarbon coolers R124 and R236ea, assuming a typical frequency $\omega_{UV} = 3 \times 10^{15}$ seg⁻¹¹² for hydrocarbons. In both cases ϕ_L^0 remains constant, as is predicted by eq 15, and ϕ_E decreases with temperature, reaching a minimum near the critical point. Furthermore, the sign of ϕ_E changes as a function of the temperature, indicating that nondispersive forces contribute favorably to the cohesive work at high temperatures, but they give rise to a slight repulsive contribution at relatively low temperatures (see Appendix I).

The values of the van der Waal distance (l) and those of ϕ_L^0 can be obtained by fitting eq 15. They are given in Table 1. The errors associated with these values are influenced by the approximation used for ω_{UV} . Figure 3 illustrates the fitting of eq 15 to the surface tension of all fluorocarbons studied (see Appendix I).

We have also studied *n*-propane (C₃), isobutane (iC₄), *n*-pentane (C₅), *n*-hexane (C₆), *n*-heptane (C₇), *n*-octane (C₈), *n*-nonane (C₉), and *n*-decane (C₁₀) using eq 15. To calculate the refractive indexes for the liquid–vapor equilibrium region, we made use of an auxiliary relation (Lorentz–Lorentz relation^{20–21}) between the density and the refractive indexes. According to this relationship the molar refractive index is given by

$$R_D = \frac{M}{\rho_L} \frac{n_L^2 - 1}{n_L^2 + 2} \quad (16)$$

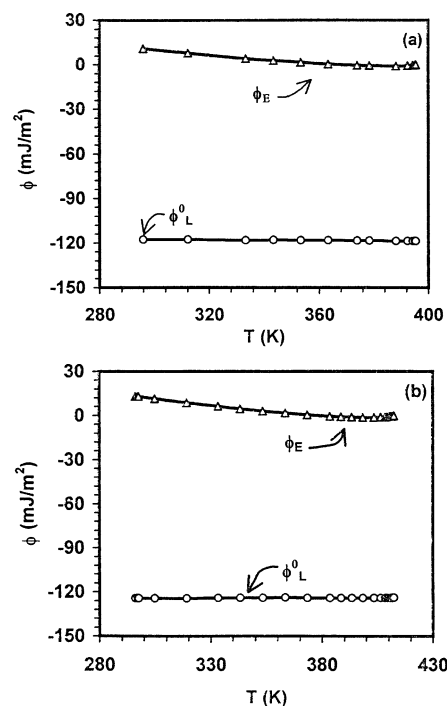


Figure 2. Surface potentials ϕ_L^0 (dispersive) and ϕ_E (nondispersive) contributing to the surface tension (eqs 10 and 15) for fluorocarbon compounds: (a) R124 and (b) R236ea.

TABLE 1: van der Waals Distance of Closest Approach l for Fluorocarbon Liquid Slabs^a

compd	$l_{vdW}/\text{\AA}$	$\phi_L^0/(\text{mJ/m}^2)$	compd	$l_{vdW}/\text{\AA}$	$\phi_L^0/(\text{mJ/m}^2)$
R143a	2.39	104.26	R245ca	2.22	134.40
R124	2.38	118.80	R236ea	2.17	123.90
E125	2.29	106.48	R236fa	2.13	119.62
R245fa	2.26	128.26			

^a Constant term (ϕ_L^0) of the dispersive contribution to the surface tension $\phi_L = \phi_L^0 + (\partial\phi/\partial T)T$ for the set of fluorocarbon compounds studied.

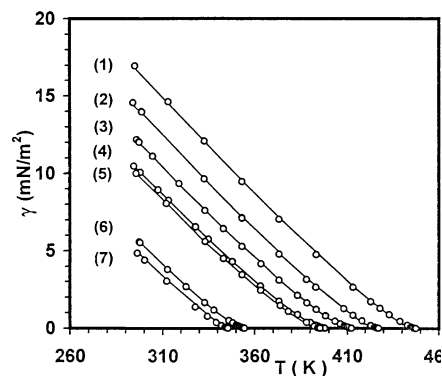


Figure 3. Dependence of the surface tension on temperature for fluorocarbons as predicted by eq 15: (1) R245ca; (2) R245fa; (3) R236ea; (4) R236fa; (5) R124; (6) E125; (7) R143.

where M is the molecular weight, ρ_L is the density of the liquid L , and n_i is the refractive index of phase i . On the other hand, if we assume $n_V^2 \approx 1$, A_{131} in eq 4b can then be written as a function of the density:

$$A_{131} \approx \frac{3h\omega_{UV}}{32\pi\sqrt{2}} \left(\frac{3\rho_L R_D}{3M + \rho_L} \right)^2 \left[\frac{2M + \rho_L R_D}{M - \rho_L R_D} \right]^{1/2} \quad (17)$$

For these calculations we used the densities reported in refs 22–29. The resulting potentials ϕ_L^0 and ϕ_E are shown in Figure

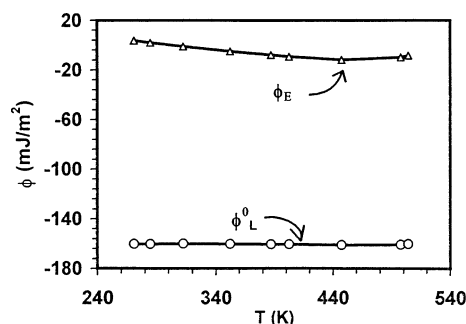


Figure 4. Surface potentials ϕ_L^0 (dispersive) and ϕ_E (nondispersive) corresponding to *n*-hexane.

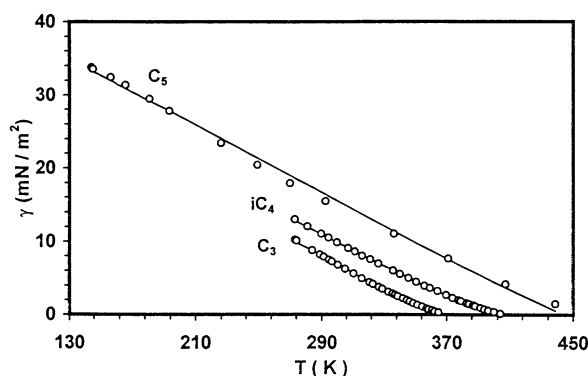


Figure 5. Surface tension of small hydrocarbons C_3 , iC_4 , and C_5 as a function of temperature, according to eq 15.

TABLE 2: Dispersive Surface Potential ϕ_L^0 and van der Waals Distance of Closest Approach l for a Selected Number of Hydrocarbon Liquids

hydrocarbon	$l_{vdW}/\text{\AA}$	$\phi_L^0/(\text{mJ}/\text{m}^2)$	hydrocarbon	$l_{vdW}/\text{\AA}$	$\phi_L^0/(\text{mJ}/\text{m}^2)$
C_3	2.52	114.46	C_7	1.67	171.70
iC_4	2.11	127.66	C_8	1.50	185.26
C_5	2.13	143.34	C_9	1.56	186.56
C_6	1.78	160.90	C_{10}	1.52	192.82

4 for the case of *n*-hexane. The behavior observed is quite similar to those of fluorocarbons (see Figure 2). Fitting of eq 15 assuming a constant value of $0.30 \text{ mJ}/(\text{m}^2 \text{ K})$ for the term enclosed by square brackets yields van der Waals distances of closest approach between the slabs (l), as well as the value of ϕ_L^0 for the hydrocarbons considered (see Table 2). The values of l obtained are in the range of interlamellar distances reported by Urbina-Villalba et al.³⁰ (from 2.07 to 1.68 Å), and those calculated by Van Oss ($1.58 \pm 0.08 \text{ \AA}$).¹⁵

Figures 5 and 6 present the fittings of eq 15 for different temperatures (data taken from refs 29, 31, and 32). Near the critical point ($T/T_c \approx 0.9$) important deviations of the expected behavior were observed, presumably due to the density fluctuations associated with the second-order transition occurring at this temperature and its effects on the calculation of A_{131}^{LW} .

Interestingly, ϕ_L^0 comes out to be linear with the critical temperature for all fluorocarbons tested (see Figure 7).

The Case of Water as a Nonpolar Compound

There are several methods available for the determination of the dispersive component of the surface tension of water. Fowkes³² estimated $\gamma^{LW} = 21.8 \text{ mJ}/\text{m}^2$ using a geometric mean of partial contributions. Good and Elbing³⁵ calculated a value of $\gamma^{LW} = 19.6 \text{ mJ}/\text{m}^2$ using molecular arguments, and also obtained γ_{ind} (induced dipole) and $\gamma_{dip-dip}$ (dipole-dipole). However, the value of $\gamma^{LW} = 21.8 \text{ mJ}/\text{m}^2$ is probably more

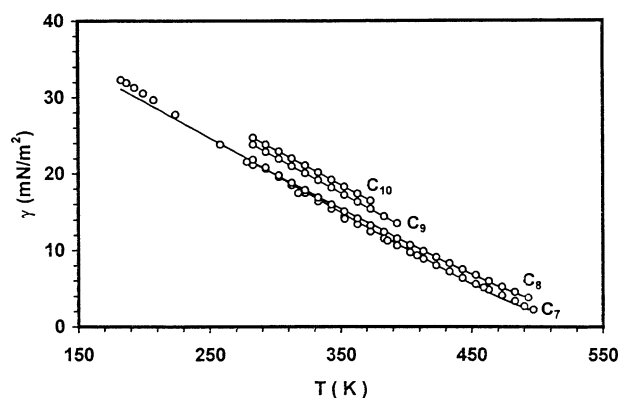


Figure 6. Surface tension of hydrocarbons C_7 – C_{10} as a function of temperature, as predicted by eq 15.

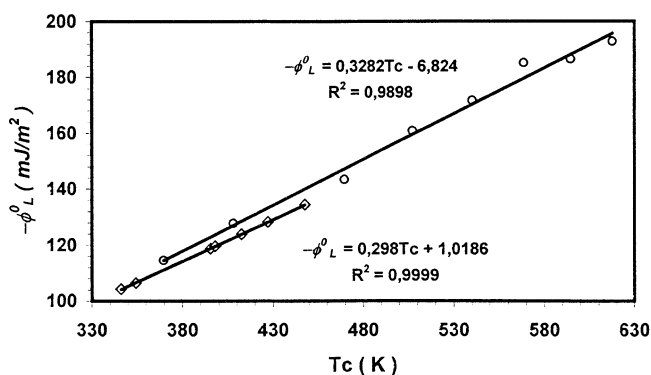


Figure 7. General relationships between ϕ_L^0 and T_c for fluorocarbon (◇) and hydrocarbon (○) compounds.

TABLE 3: van der Waals Distance of Closest Approach Calculated for Water on the Basis of Dispersive Contributions Only^a

Hamaker constant for H_2O , $A_{131}/\text{mJ} \times 10^{17}$	$l_{vdW}/\text{\AA}$		ref
	fluorocarbons	hydrocarbons	
3.94	1.31	1.20	36
4.62	1.42	1.30	15
5.01	1.48	1.35	7
5.72	1.58	1.45	6
5.50	1.55	1.42	8

^a The values of the Hamaker constant as well as their respective references are listed in columns 1 and 4.

widely used and was employed by Van Oss et al.¹⁵ in their description of polar and nonpolar contributions of this molecule.

In principle there is no reason to expect that the nonpolar component of the surface tension of water should have a dependence on temperature similar to that observed in fluorocarbons and hydrocarbons. However, if this hypothesis is assumed, the potential ϕ_L^0 may be estimated from the variation of this potential with the critical temperature ($T_c^{\text{water}} = 647.1 \text{ K}$). Using fluorocarbon data, a value of $-193.85 \text{ mJ}/\text{m}^2$ is obtained, while $-205.5 \text{ mJ}/\text{m}^2$ results using hydrocarbon data. On the other hand, the values of l can be calculated using eq 15 (with $\gamma^{LW} = 21.8 \text{ mJ}/\text{m}^2$) and the value of A_{131} reported by several authors (refs 6–8, 15, 34, and 35). As shown in Table 3, the best values of l correspond to those values of the Hamaker constant more rigorously determined.

Conclusions

(1) The reversibility requirement for the calculation of the cohesive work of fluorocarbons and hydrocarbons requires account of nondispersive forces along with dispersive ones.

However, the magnitude of nondispersive contributions is at least 1 order of magnitude smaller. The contribution of nondispersive forces (weighted by ϕ_E) to the cohesive work can be positive or negative depending on the temperatures. Decomposition of the surface tension into these surface contributions (ϕ_L and ϕ_E) allows simple descriptions of the dependence of γ_{13} on temperature.

(2) Depending on the experimental data available, the equations forwarded can be used to relate the Hamaker constant to the distance of closest approach between slabs of molecules, and their surface tension. It was shown how van der Waals distances can be obtained by fitting experimental data on the variation of the tension with the temperature for all fluorocarbon and hydrocarbon fluids studied. Furthermore, a linear relation between ϕ_L^0 and T_c was obtained for each series of molecules. This is complementary to the linear dependence of the complete dispersive potential $\phi_L = \phi_L^0 + (\partial\phi/\partial T)T$ with T .

(3) Simple empirical relations such as the ones described above allow the temperature dependence of the flocculation rate of aerosols to be studied, and can probably be applied to evaluate the aggregation rate of liquid dispersions by means of Brownian dynamics simulations.³⁷

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Appendix I: Entropic Contributions and the Value of Φ_E

The approximations used in this work to evaluate the Hamaker function (in the framework of Lifshitz's theory) are basically associated with (a) the mathematical procedures required for the simplification of eq 2 and (b) the characteristic absorption spectra and refractive index of the interacting media. The present approach is empirical: it evaluates the van der Waals contributions coming from Lifshitz theory, and assigns the rest of the contributions (see eq 7) to the function Φ_E .¹⁵ As pointed out by one of the reviewers, this empirical procedure does not evidence the dramatic change in the orientation of hydrocarbons and fluorocarbons with temperature that occurs at the interface. Such changes generate a discrepancy between Lifshitz theory and the experiment that is not clearly appreciated through the variation of Φ_E with temperature.

Several years ago Good³⁸ proposed that the surface entropy of a liquid may be taken as a criterion of surface orientation. The surface entropy is equal to the differential of the surface tension with respect to temperature. Since the surface tension of hydrocarbons changes linearly with temperature, their surface entropy has a constant value for each alkane which decreases monotonically with the number of carbons.³⁹ Figure 8 shows the surface entropy of two fluorocarbons (Figure 8a,b) and two hydrocarbons (Figure 8c,d) of different lengths. This entropy was calculated from surface tension data and is represented by black dots (s^σ). The entropic contributions coming from Φ_E and Lifshitz–van der Waals interaction are identified by s^E and s^{LW} , respectively. These values were calculated by numerical differentiation of their respective free energies with respect to temperature. As is clear from this figure, Lifshitz theory goes the wrong way as compared with experiment for all molecules presented. As indicated by the reviewer, it is easy to get free energies but hard to get entropy and enthalpy, which tell what is really going on in the surface.

Figure 9 shows the absolute deviation of the surface tension of the studied fluorocarbons as a function of the reduced temperature (T_r). The errors are less than 0.20 mN/m in all cases.

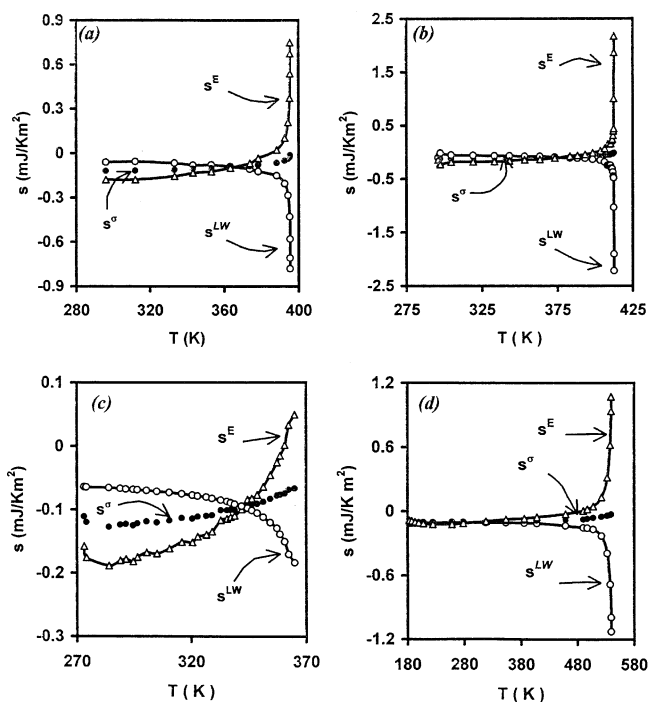


Figure 8. Surface entropy contributions to the surface free energy for (a) R124, (b) R236ea, (c) propane, and (d) *n*-heptane. The black dots correspond to the experimental entropy calculated from the variation of the surface tension with temperature (s^σ). Empty triangles indicate the variation of the nondispersive contributions as a function of temperature. Empty circles indicate the Lifshitz–van der Waals contribution.

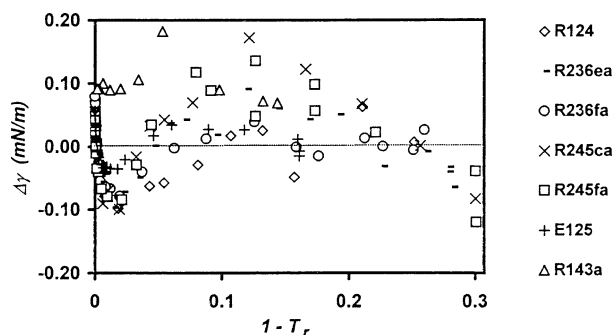


Figure 9. Absolute errors in the surface tension calculated from eq 15.

This limit is rather large when compared to some empirical predictions based on the law of corresponding states.² The purpose of the present work was to study the variation of the Hamaker function with respect to temperature. In a future paper we will show how the law of corresponding states can be used along with the theory described in refs 17 and 18 to obtain deviations of less than 0.5% in the prediction of the interfacial tension.

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