

## Letters

### Fluorocarbons: Surface Free Energies and van der Waals Interaction

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Surface free energies have been calculated for solid fluorocarbon materials by employing a method that utilizes dielectric data and theoretical predictions of van der Waals (dispersion) interactions. Excellent agreement between the results of direct force measurements and those of the theory for retarded van der Waals interactions supports the methodology. Two relatively new fluorocarbon polymers have been identified as having the lowest known surface free energies of all bulk homogeneous polymeric solids. This study provides confirmation that estimates of solid surface free energies based on contact angle measurements with dispersive organic liquids depend on the dielectric properties of both the liquids and the solid.

Since the discovery of poly(tetrafluoroethylene), over fifty years ago,<sup>1</sup> there has been a great deal of developmental work aimed at optimizing the use of fluorocarbon polymers as ultra low-adhesive (optimally "non-stick") materials. Among similar classes of dispersive materials, the surface free energy per unit area of a solid organic material can be used as a simple guide to its relative adhesive properties. However, it is not a straightforward exercise to measure directly the surface free energies of nonelastomeric solids. This has led to the surface free energies of dispersive solids frequently being compared by using procedures that are based on contact angle ( $\theta$ ) measurements. Zisman critical surface tensions ( $\gamma_c$ ) and surface tensions derived from the Good–Girafalco–Fowkes equation ( $\gamma_{\text{GGF}}$ ) are regularly quoted as measures of the surface free energies of organic solids. The critical surface tension defines the wettability of a solid by noting the lowest surface tension a liquid can have and still exhibit a contact angle greater than zero degrees on that solid.<sup>2</sup> The  $\gamma_c$  of a surface is usually obtained from a

Zisman plot of contact angles; i.e. a plot of  $\cos \theta$  versus the surface tensions of dispersive liquids ( $\gamma_{\text{LV}}$ ) with the extrapolation of  $\gamma_{\text{LV}}$  to  $\cos \theta = 1$  giving  $\gamma_c$ . There is no theoretical justification for equating the critical surface tension with the surface free energy of a material.<sup>2</sup> The Good–Girafalco–Fowkes equation has the form<sup>3,4</sup>

$$\gamma_{\text{GGF}} = \gamma_{\text{LV}}((\cos \theta + 1)/2)^2 \quad (1)$$

This equation is generally utilized either by substituting the  $\gamma_{\text{LV}}$  and  $\theta$  values for a single dispersive liquid into the equation to yield  $\gamma_{\text{GGF}}$  or by plotting  $\cos \theta$  versus  $(1/\gamma_{\text{LV}})^{1/2}$  for a family of dispersive liquids (normally alkanes) with the ordinate of the best linear fit being  $-1$  and the gradient giving  $2(\gamma_{\text{GGF}})^{1/2}$ . A theoretical justification has been provided for the Good–Girafalco–Fowkes equation.<sup>4</sup> Nevertheless, this justification is reliant on the validity of several assumptions including that the van der Waals (dispersion) interaction is governed by the ultraviolet (UV) part of the dielectric permeability function and that the

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(2) Zisman, W. A. *Ind. Eng. Chem.* **1963**, *55*, 18.

(3) Girafalco, L. A.; Good, R. J. *J. Phys. Chem.* **1957**, *61*, 904. Good, R. J.; Girafalco, L. A. *J. Phys. Chem.* **1960**, *64*, 561.

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interacting solid and liquids absorb at similar frequencies in the UV region (see below).<sup>4,5</sup>

Here we take a different approach and use a relationship between the surface free energy (surface tension) of perfluoro liquids and the nonretarded Hamaker constant, that characterizes van der Waals interaction at surface contact, as input to determine the surface free energies of several solid perfluorocarbon polymers. The solid surface free energies are compared with other estimates including  $\gamma_c$  and  $\gamma_{GGF}$  values.

The work of cohesion for a homogeneous material (or alternatively the reversible work required to create new surfaces by cleaving a homogeneous material) may be expressed as<sup>2</sup>

$$W_c = 2\gamma \quad (2)$$

where  $\gamma$  is the surface free energy per unit area of the material. The van der Waals free energy of interaction per unit area ( $E_{121}(H)$ ) for two planar similar surfaces at a separation  $H$  may be expressed as<sup>5-9</sup>

$$E_{121}(H) = \frac{-A_{121}(H)}{12\pi H^2} \quad (3)$$

where  $A_{121}(H)$  is the Hamaker function that is governed by the dielectric properties of the two interacting similar materials (1) and the intervening medium (2). When cohesion is governed solely by van der Waals interaction, it is frequently assumed that  $W_c$  is equal to  $E_{121}$  at contact separation  $H_0$ , where the intervening medium is vacuum (air).<sup>5-9</sup> Therefore, the surface free energy per unit area (surface tension) of an inert dispersive fluorocarbon material can be considered to be half the cohesive energy of the material so that

$$\gamma_d = \frac{-A_{FVF}(H_0)}{24\pi H_0^2} \quad (4)$$

where  $A_{FVF}(H_0)$  is the nonretarded Hamaker constant (i.e. the value of the Hamaker function,  $A_{FVF}(H)$ , at surface contact) for the homo-interaction of the fluorocarbon material across a vacuum.<sup>10</sup>

In this work, we calculate the  $A_{FVF}(H_0)$  for seven perfluoro liquids of known surface tension. We use eq 4 to derive the  $H_0$  values for these liquids. On the basis of

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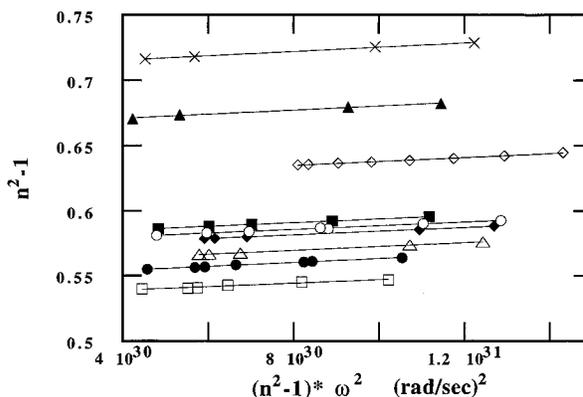
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(10) In this paper we have followed the normal convention<sup>5-9</sup> and ignored the very short-range Born repulsion. Incorporation of this component would change the individual values of  $H_0$  slightly but would not change any of the general conclusions, including the calculated surface free energies. It should be borne in mind that at separations less than a few angstroms the graininess of matter becomes important and therefore  $H_0$  values derived in this work should be viewed as semiempirical values without real physical significance.<sup>7</sup> It is also implicit to our treatment that the surface can be described by bulk material properties (i.e., it is assumed that molecules do not acquire a specific orientation at the surface).<sup>7</sup>



**Figure 1.** Cauchy plots for perfluorocarbon materials: (□) *n*-pentane; (○) cyclopentane; (●) 2-methylbutane; (△) *n*-hexane; (◆) 2-methylpentane; (■) *n*-heptane; (◇) 2-butyltetrahydrofuran; (×) Teflon AF 1600; (▲) Teflon AF 2400. The axis of the ordinate intercept gives  $C_{UV}$ , and the gradient gives  $1/\omega_{UV}^2$ .

the assumption that material density and  $H_0$  are related,<sup>8,9</sup>  $H_0$  estimates and calculated  $A_{FVF}(H_0)$  values are employed to determine the surface free energies of two relatively new amorphous copolymers of perfluoro(2,2-dimethyl-1,3-dioxole) and tetrafluoroethylene (Teflon AF 1600 and Teflon AF 2400, where the ratio of dioxole to TFE is 66:34 and 84:16, respectively). The same procedure is employed to determine the lower boundaries for the surface free energies of both low-density (LD) and high-density (HD) poly(tetrafluoroethylene) (PTFE). In addition, an atomic force microscope is used to directly measure the van der Waals interaction between two Teflon AF 1600 surfaces across air, and these results are compared with the calculated behavior.

Nonretarded Hamaker constants, and full Hamaker functions where necessary (see below), were calculated from Lifshitz theory.<sup>11</sup> The nonretarded Hamaker constant for the interaction between similar half-spaces with dielectric permeability  $\epsilon_1(\omega)$  across an intervening medium of dielectric permeability  $\epsilon_2(\omega)$  is given by

$$A_{121}(H_0) = \frac{3k_B T}{2} \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \frac{(\Delta_{12}^s)^2}{s^3} \quad (5)$$

where

$$\Delta_{12} = \frac{\epsilon_1(i\xi_n) - \epsilon_2(i\xi_n)}{\epsilon_1(i\xi_n) + \epsilon_2(i\xi_n)} \quad (6)$$

and

$$\xi_n = (4\pi^2 k_B T/h)n \quad (7)$$

The prime on the summation in eq 5 denotes that the term at zero frequency ( $n = 0$ ) is given half weight.  $k_B$ ,  $T$ , and  $h$  denote the Boltzmann constant, absolute temperature, and Planck's constant, respectively.  $\epsilon(\omega)$  is dealt with as a function of the complex variable  $\omega$  only on the imaginary axis  $\omega = (i\xi)$ . The Ninham-Parsegian representation<sup>12</sup> of the dielectric permeability as a function of imaginary frequency  $i\xi$  was used with

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**Table 1. Physicochemical Properties of the Perfluorocarbon Materials at  $20 \pm 2$  °C**

property <sup>a</sup>	pen- tane <sup>b</sup>	cyclo- pentane <sup>b</sup>	2-methyl- butane <sup>b</sup>	hexane	2-methyl- pentane	heptane	2-butyltetra- hydrofuran	AF1600	AF2400	PTFE	
										LD	HD
$\rho$ (g cm <sup>-3</sup> )	1.6367	1.6602	1.6805	1.6995	1.7326	1.7318	1.77	1.78	1.67	2.1	2.3
$\epsilon_0$	1.72	1.76	1.73	1.74	1.76	1.765	1.86	1.934	1.904	2.0	2.1
$n_D$	1.2412	1.2581	1.2474	1.2515	1.2564	1.2602	1.276	1.3122	1.2947	1.3434	1.3801
$C_{UV}$	0.533	0.574	0.548	0.557	0.570	0.579	0.623	0.709	0.665	0.792	0.890
$10^{-16} \omega_{UV}$ (rad s <sup>-1</sup> )	2.602	2.648	2.571	2.572	2.630	2.620	2.593	2.457	2.522	2.654	2.640
$C_{IR}$	0.186	0.186	0.186	0.186	0.186	0.186	0.237	0.225	0.239	0.21	0.21
$10^{-14} \omega_{IR}$ (rad s <sup>-1</sup> )	2.356	2.356	2.356	2.356	2.356	2.356	2.356	2.356	2.356	2.356	2.356
$10^{20} A_{FVF}(H_0)$ (J)	2.594	2.990	2.685	2.763	2.933	3.001	3.357	3.92	3.63	5.05	6.02
$10^{21} A_{FWF}(H_0)$ (J)	4.370	3.910	4.194	4.085	3.943	3.870	3.632	3.59	3.55	5.24	7.39
$\gamma_d$ (mN m <sup>-1</sup> )	10.33	11.59	10.94	11.4/11.92	12.38	12.5/12.96	15.12	16.4 ± 1.4	15.2 ± 1.3	>22.9	>27.3
$H_0$ (nm)	0.183	0.185	0.180	0.179/0.175	0.177	0.178/0.175	0.172	0.178 ± 0.007	0.178 ± 0.007	<0.171	<0.171

<sup>a</sup>  $\rho$ : density.  $\epsilon_0$ : static dielectric constant.  $n_D$ : refractive index at a wavelength of 589 nm.  $C_{UV}$  and  $C_{IR}$ : effective oscillator strengths of the ultraviolet (UV) and infrared (IR) absorption bands.  $\omega_{UV}$  and  $\omega_{IR}$ : frequencies of the UV and IR absorption band maxima.  $A_{FVF}(H_0)$  and  $A_{FWF}(H_0)$ : nonretarded Hamaker constants for homo-interaction across vapor (air) and water (the Gingell–Parsegian representation<sup>9</sup> for the water dielectric permeability function was used).  $\gamma_d$ : surface free energy, which is known for the liquids (surface tension) and calculated for the solids, viz. Teflon AF 1600, Teflon AF 2400, and low-density and high-density PTFE.  $H_0$ : surface separation at contact (see eq 4), which is calculated for the liquids and inferred for the solids (see text). <sup>b</sup> Because of the low boiling points, the dielectric properties and  $\gamma_d$  refer to 15 °C.

$$\epsilon(i\xi) = \epsilon_0, \quad \text{when } \xi = 0$$

$$\epsilon(i\xi) = 1 + \frac{C_{IR}}{1 + (\xi/\omega_{IR})^2} + \frac{C_{UV}}{1 + (\xi/\omega_{UV})^2}, \quad \text{when } \xi > 0 \quad (8)$$

where  $\epsilon_0$  is the static dielectric constant,  $\omega_{IR}$  and  $\omega_{UV}$  are the frequencies of the infrared (IR) and ultraviolet (UV) absorption band maxima, and  $C_{IR}$  and  $C_{UV}$  are related to the oscillator strengths of the absorption bands. The procedure of Hough and White was employed to obtain the representations of the dielectric permeability functions.<sup>8</sup> The  $C_{UV}$  and  $\omega_{UV}$  values for the materials were determined from Cauchy plots of refractive index ( $n$ ) data from the low-frequency side of the ultraviolet absorption, where the extinction coefficient is negligible. It was assumed that

$$C_{IR} = \epsilon_0 - C_{UV} - 1 \quad (9)$$

For the perfluorocarbon materials, refractive indices as a function of wavelength in the visible region were obtained from several literature sources.<sup>13</sup> Cauchy plots for the seven perfluoro liquids and the two perfluoro copolymers (Figure 1) show very good linearity. The PTFE  $C_{UV}$  and  $\omega_{UV}$  values were derived from the optical data for perfluorohexane and perfluoroheptane. The UV part of the dielectric response for low-density (LD) and high-density (HD) PTFE was constructed by using the Lorenz–Lorentz equation to obtain refractive indices in the visible part of the absorption spectrum,  $n_\lambda$ .<sup>14</sup>

$$n_\lambda = \left( \frac{1 + 2R_L(\rho/M)}{1 - R_L(\rho/M)} \right)^{1/2} \quad (10)$$

where  $R_L$  is the molar refraction of the PTFE repeat unit ( $-CF_2-$ ) and is a function of wavelength  $\lambda$ ,  $\rho$  is the density, and  $M$  is the molecular weight of the repeat unit. The molar refraction for the PTFE repeat unit was calculated

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(14) Born, M.; Wolf, E. *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 3rd ed.; Pergamon Press: Oxford, 1965. Specifically,  $n_\lambda$  values were obtained at 436, 486, 546, 589, and 656 nm.

by determining the molar refraction of perfluoroheptane and perfluorohexane at each of the selected wavelengths. It was assumed that the difference between the  $R_L$  values for these two perfluoro liquids was the molar refraction for the PTFE repeat unit at the wavelength of interest.<sup>14</sup> Cauchy plots were then used to obtain the  $C_{UV}$  and  $\omega_{UV}$  values for LD and HD PTFE. Hough and White have reported<sup>8</sup> PTFE  $C_{UV}$  and  $\omega_{UV}$  values derived from Rance's experimental refractive index data in the visible region.<sup>15</sup> We have found that their  $\omega_{UV}$  value of  $1.793 \times 10^{16}$  rad s<sup>-1</sup> is not consistent with that of a perfluorocarbon material (see Table 1). We are unaware of any high-quality experimental refractive index data for PTFE in the visible region.

The physicochemical properties for the perfluorocarbon materials are given in Table 1. The list includes the density ( $\rho$ ), the refractive index at the sodium D line ( $n_D$ ), dielectric permeability data ( $\epsilon_0$ ,  $C_{IR}$ ,  $\omega_{IR}$ ,  $C_{UV}$ , and  $\omega_{UV}$ ), nonretarded Hamaker constants across both air ( $A_{FVF}(H_0)$ ) and water ( $A_{FWF}(H_0)$ ), and the liquid/vapor surface tension ( $\gamma_d$ ). The primary data were obtained from several sources.<sup>13,16–18</sup> It is generally accepted that modern theory can predict the nonretarded Hamaker constant to within 10%.<sup>8</sup> Specifically in the case of the homo-interaction of crystalline quartz (which has a far more complicated UV

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(17) The surface tension of perfluoro-2-butyltetrahydrofuran was determined experimentally by the du Nouy ring technique. For the perfluoro liquids we could only find  $\epsilon_0$  values for heptane and 2-butyltetrahydrofuran. Therefore, for the other perfluoroalkanes it was assumed that  $C_{IR} = 0.186$  and eq 9 could be used to calculate  $\epsilon_0$ . The Hamaker constant calculations are not sensitive to small changes in  $\epsilon_0$  and  $C_{IR}$ .

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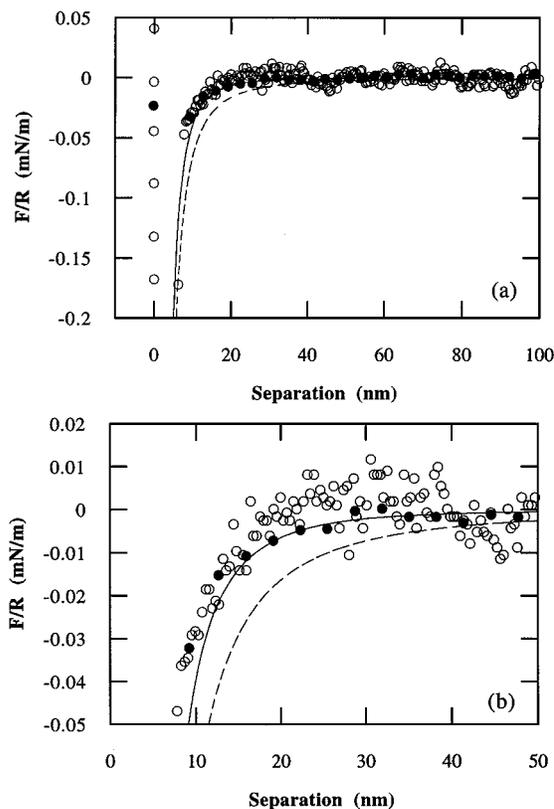
absorption spectrum than the perfluorocarbons) across air, it has been shown that the simple method of the  $\epsilon(i\xi)$  construction, as employed above, provides a Hamaker constant that differs by 4% from the most accurate  $\epsilon(i\xi)$  available, constructed from energy loss data.<sup>8</sup>

Table 1 contains inferred  $H_0$  values obtained when the Hamaker constant,  $A_{FVF}(H_0)$ , calculated from Lifshitz theory and the experimental surface tension,  $\gamma_0$ , of the perfluoro liquids is substituted into eq 4. For some of the perfluoro liquids there is variation in the reported surface tension value. Therefore, for these liquids more than one  $\gamma_d$  and  $H_0$  value is listed in Table 1. Hough and White have shown for linear alkanes, pentane to hexadecane, that  $H_0$  is a function of  $\rho^{-1/2}$ .<sup>8</sup> For the perfluorocarbon materials there is not a well-defined relationship, due to the spread of the experimentally obtained  $\gamma_d$  values, but there is a general trend of a decrease in  $H_0$  as  $\rho$  increases.

As the Teflon AF 1600 and Teflon AF 2400 polymers are amorphous and have densities in the same range as the perfluoro liquids, the average  $H_0$  value obtained for the perfluoro liquids was substituted into eq 4 together with the Teflon AF Hamaker constants,  $A_{FVF}(H_0)$ , calculated from Lifshitz theory to obtain the surface free energy per unit area ( $\gamma_d$ ). PTFE Hamaker constants and lower limits for  $\gamma_d$ , calculated by employing eq 4, are also included in Table 1. The assumption was that, because the densities of LD and HD PTFE are greater than those of any of the other perfluorocarbon materials,  $H_0$  would be smaller than the lowest value found for the other materials.

The calculated  $\gamma_d$  estimates for PTFE are consistent with some other estimates of surface free energy. On the basis of a temperature extrapolation of the surface tension data of a PTFE melt, the solid surface free energy can be estimated to be  $23.9 \text{ mN m}^{-1}$ .<sup>19</sup> An extrapolation of the surface tension data for perfluoroalkane liquids to infinite chain length gives a surface free energy of  $25.6 \pm 0.6 \text{ mN m}^{-1}$ .<sup>20</sup> The Good–Girafalco–Fowkes equation<sup>3,4</sup> gives  $\gamma_{GGF} = 24.5 \text{ mN m}^{-1}$  for a system using the advancing contact angle formed by a perfluorocarbon liquid on the surface of PTFE,<sup>21–23</sup> but when the linear alkane series from hexane to hexadecane is used as the test liquids, it has been found that  $\gamma_{GGF} = 19.5 \text{ mN m}^{-1}$  and  $\gamma_c = 18.6 \text{ mN m}^{-1}$ .<sup>4,22</sup>

The Teflon AF polymers are relatively new and, to our knowledge, there has been no other estimation of their surface free energies. Advancing contact angles were measured with linear alkanes, pentane to hexadecane, to obtain the  $\gamma_c$  (Zisman plots)<sup>2</sup> and  $\gamma_{GGF}$  values for Teflon AF 1600 and Teflon AF 2400;<sup>24</sup>  $\gamma_c$  equals 12.1 and 11.9



**Figure 2.** Force of interaction between a sphere and flat plate, normalized by the radius of the sphere ( $R$ ), as a function of the separation of closest approach. The interaction is across air and between Teflon AF 1600 surfaces. Results are presented for two separate experiments with  $R = 2.9 \mu\text{m}$  (○) and  $5.1 \mu\text{m}$  (●). The dashed line is the calculated nonretarded van der Waals interaction (Hamaker constant  $A_{FVF}(H_0) = 3.9 \times 10^{-20} \text{ J}$ ). The solid line is the calculated retarded van der Waals interaction (using the full Hamaker function,  $A_{FVF}(H)$ ). Part of the force–separation curve shown in part a is expanded in part b in order to facilitate the comparison between theory and experiment.

$\text{mNm}^{-1}$  for Teflon AF 1600 and Teflon AF 2400, respectively, while  $\gamma_{GGF}$  equals 13.9 and  $13.8 \text{ mN m}^{-1}$ . As was the case with PTFE,  $\gamma_c$  and  $\gamma_{GGF}$  are significantly lower than the calculated surface free energies  $\gamma_d$ . Contact angle measurements of perfluorocarbon liquids on Teflon AF surfaces present experimental difficulties.<sup>24</sup>

There have been reports that  $\gamma_{GGF}$  values give a reasonable estimate of the  $\gamma_d$  of solids, providing both the liquids and solids belong to the same class of dispersive materials (either hydrocarbon or fluorocarbon).<sup>4,25</sup> Consistent with the work presented here, it has also been reported that  $\gamma_{GGF}$  values obtained with liquid alkanes give marked underestimates of the  $\gamma_d$  of fluorocarbon materials.<sup>4,25</sup> The derivation of the Good–Girafalco–Fowkes equation is reliant on a number of assumptions, including that  $\omega_{UV}$  values are similar for the two interacting materials.<sup>4,5</sup> The present work indicates that the fluorocarbon  $\omega_{UV}$  values (Table 1) are significantly larger than the liquid alkane  $\omega_{UV}$  of  $(1.86 \pm 0.02) \times 10^{16} \text{ rad s}^{-1}$ .<sup>8</sup>

Contact load deformation experiments with self-assembled monolayers of fluoroalkylsiloxane on surface-oxidized elastomeric polydimethylsiloxane (PDMS<sup>ox</sup>– $\text{O}_3\text{Si}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$ ) have provided a  $\gamma_d$  of  $16 \pm 0.5 \text{ mN}$

obtained for high-purity  $\text{C}_5$ – $\text{C}_{16}$  alkanes. Teflon AF 1600 and AF 2400 surfaces had  $\theta_A$  values of  $120^\circ$  and  $125^\circ$ , respectively, for water. Perfluorodecalin ( $\gamma_{LV} = 18.2 \text{ mN m}^{-1}$ ) was also placed on the Teflon AF surfaces, but reliable contact angles could not be obtained because the liquid rapidly penetrated the surface.

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(21) This estimate for the PTFE surface free energy was determined by using the Good–Girafalco–Fowkes equation,<sup>3,4</sup> eq 1, and the contact angle ( $\theta < 5^\circ$ ) for a perfluorinated aliphatic hydrocarbon ( $\gamma_{LV} = 24.6 \text{ mN m}^{-1}$ ) from ref 22.

(22) Fox, H. W.; Zisman, W. A. *J. Colloid Sci.* **1950**, *5*, 514.

(23) If we take the average value of these three experimental estimates of the surface free energy for PTFE,  $24.7 \pm 1.8 \text{ mN m}^{-1}$ , and assume that they refer to low-density material, then the  $H_0$  for LD PTFE can be calculated as  $0.165 \pm 0.005 \text{ nm}$ .

(24) A solution of Teflon AF (Dupont Polymer Products; Wilmington, DE) was prepared by dissolving Teflon AF prills (2 wt %) in perfluoro-2-butyltetrahydrofuran (Fluoroinert liquid FC75, 3M Australia Pty. Ltd) at  $50^\circ\text{C}$ . Thin films of Teflon AF were cast from the fluorocarbon solutions onto freshly cleaved mica surfaces and allowed to stand overnight before being placed in an oven at  $100^\circ\text{C}$  for a further 2 h. The resultant Teflon AF films were transparent. AFM (Nanoscope III, Digital Instruments, CA) images ( $1.0 \mu\text{m}^2$ ) of the coatings on mica showed that the Teflon AF 1600 and AF 2400 coatings had root mean square (rms) roughnesses of 0.3 and 0.4 nm, with some features up to 3 and 4 nm in height, respectively. Advancing ( $\theta_A$ ) contact angles were

$m^{-1}$ .<sup>25</sup> For homogeneous perfluorocarbon materials of similar  $\omega_{UV}$  there is a correlation between  $C_{UV}$  ( $\approx n_D^2 - 1$ ) and  $\gamma_d$  (Table 1). The Teflon AF  $n_D$  values are, to our knowledge, the lowest of all bulk homogeneous organic polymeric solids and are very close to the theoretical lower limit.<sup>26</sup> Therefore, by inference, the surface free energy  $\gamma_d$  should also be the lowest. It is reassuring to note that the  $\gamma_d$  values we calculated for the Teflon AF materials are similar to those for the fluoroalkyl-modified PDMS surface.

An independent assessment of the calculated van der Waals interaction for perfluorocarbons was performed. An atomic force microscope (AFM) was used to measure the force of interaction across air between a sphere and a flat plate both coated with Teflon AF 1600.<sup>27,28</sup> The Derjaguin approximation<sup>29</sup> allows the interaction force between the sphere and the flat plate ( $F$ ) to be related to the interaction energy per unit area between two planar surfaces ( $E$ ) with

$$E = \frac{F}{2\pi R} \quad (11)$$

(26) Groh, W.; Zimmermann, A. *Macromolecules* **1991**, *24*, 6660.

(27) The use of the AFM (Nanoscope III; Digital Instruments, CA) to quantitatively measure the force of interaction between a sphere and a flat plate has been reported in several recent works. For experimental details see, for example: Ducker, W. A.; Senden, T. J.; Pashley, R. M. *Langmuir* **1992**, *8*, 1831. Larson, I.; Drummond, C. J.; Chan, D. Y. C.; Grieser, F. *J. Am. Chem. Soc.* **1993**, *115*, 11885. Drummond, C. J.; Senden, T. J. *Colloids Surf., A* **1994**, *87*, 217. The measured force of interaction is considered to have an accuracy of  $\pm 20\%$ , with the major uncertainty ( $\pm 15\%$ ) arising from the experimental determination of the v-shaped cantilever spring constant ( $k$ ). The surfaces generally used in AFM force measurements are too rough and inelastic to get a quantitative value for the reversible work of adhesion.

(28) Small glass spheres, in the micron size range, attached to v-shaped cantilevers ( $k = 0.33 \pm 0.05$ ), and oxidized silicon wafers were reacted with [(heptafluoroisopropoxy)propyl]methylchlorosilane vapor, at room temperature and pressure, for approximately 30 min and then left for at least a day in a dust free environment. The fluoro-silanated glass spheres were coated with Teflon AF 1600 by dipping them in a 0.1 wt % solution of Teflon AF in perfluoro-2-butyltetrahydrofuran. The fluoro-silanated wafer was coated with Teflon AF 1600 by casting a thin film from the same solution. The fluoro-silanation step was necessary in order to get good adhesion of the Teflon AF coatings to the substrates. The coated surfaces were left to dry at room temperature for at least 3 days before AFM experiments were performed. The coated wafer (rms roughness of 0.5 nm with a few features up to 4 nm in height over a  $1.0 \mu\text{m}^2$  area) was less rough than the native oxidized wafer (rms roughness of 0.8 nm with a few features up to 10 nm).

(29) Derjaguin, B. V. *Kolloid Z.* **1934**, *69*, 155.

where  $R$  is the radius of the sphere. Utilizing the relationships in eqs 3 and 11, we obtain for the van der Waals interaction between fluorocarbon surfaces

$$\frac{F}{R} = \frac{-A_{FVF}(H)}{6H^2} \quad (12)$$

Figure 2 compares two separate experiments for spheres of radius 2.9 and 5.1  $\mu\text{m}$  with two theoretical curves described by eq 12. The two experiments give concordant results. The two theoretical curves correspond to non-retarded and retarded van der Waals interaction.<sup>11</sup> Retardation of the van der Waals interaction is expected at separations greater than  $H_0$ .<sup>9</sup> Given the accuracy of the force measurement<sup>27</sup> and that one would expect some attenuation of the interaction at close separations due to surface roughness, there is excellent agreement between the measured retarded van der Waals interaction and that calculated from a theoretical consideration of the dielectric properties.

In this report, we have (i) obtained accurate dielectric data to facilitate the determination of van der Waals interactions involving perfluorocarbon materials which are important candidates for the design of low surface free energy "nonstick" surfaces; (ii) suggested that the calculated surface free energy  $\gamma_d$  has good theoretical justification to be used as a criterion for selecting such materials; (iii) noted that the much used method of estimating surface free energies based on contact angle measurements with dispersive organic liquids should be used with caution as the results obtained depend on the dielectric properties of both the liquids and the solid; (iv) identified the relatively new perfluorocarbon solids, Teflon AF1600 and Teflon AF2400, as having the lowest known surface free energies of all bulk homogeneous polymeric solids; and (v) found that theoretical predictions of retarded van der Waals interactions are in excellent agreement with direct force measurements, which provides support for our analysis.

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