

van der Waals Interaction, Surface Free Energies, and Contact Angles: Dispersive Polymers and Liquids

Calum J. Drummond*[†] and Derek Y. C. Chan[‡]

CSIRO Division of Chemicals and Polymers, Private Bag 10, Clayton South MDC, Clayton, Victoria 3169, Australia, and Department of Mathematics, The University of Melbourne, Parkville, Victoria 3052, Australia

Received December 27, 1996. In Final Form: April 14, 1997[Ⓢ]

The Lifshitz theory of van der Waals interaction has been employed to calculate the contact angles of diiodomethane, 1-bromonaphthalene, 1-methylnaphthalene, bromobenzene, 1-*tert*-butylnaphthalene, liquid paraffin, and hexadecane on poly(dimethylsiloxane), poly(4-methyl-1-pentene), polyethylene, natural rubber, and polystyrene surfaces. The theoretical treatment is based on the equation $\cos \theta = [(2A_{PVL}/A_{LVL}) - (H_{0LVL}/H_{0PVL})^2] - 1$, where θ is the contact angle and A_{PVL} and A_{LVL} are the non-retarded Hamaker constants for the heterointeraction between polymer and liquid across vacuum and the homo interaction of the liquid across vacuum, respectively. Nonretarded Hamaker constants have been determined from the dielectric properties of the materials and application of the Lifshitz theory. H_{0LVL} and H_{0PVL} are the equilibrium "contact" surface separations associated with the liquid–liquid homointeraction and polymer–liquid heterointeraction across vacuum, respectively. H_{0LVL} values, and the analogous H_{0PVP} values associated with polymer homointeraction, have been estimated from the surface free energies of the dispersive liquids and polymers. Four different approaches, each with a different assumption regarding the heterointeraction between polymer and liquid, have been used to obtain H_{0PVL} values: (i) $H_{0PVL} = H_{0LVL}$, (ii) $H_{0PVL} = H_{0PVP}$, (iii) a geometric mean relationship, $H_{0PVL} = (H_{0PVP}H_{0LVL})^{1/2}$, and (iv) an arithmetic mean relationship, $H_{0PVL} = (H_{0PVP} + H_{0LVL})/2$. Theoretical contact angles obtained with the four approaches have been compared with experimental contact angles. In general, the approaches which employ the combining rules, whether geometric or arithmetic, provide the best agreement between theory and experiment. Previous work that has dealt with the contact angles of *n*-alkanes on poly(tetrafluoroethylene) has also been re-examined. For the perfluorocarbon–hydrocarbon system none of the approaches are able to reconcile theory and experiment.

Introduction

The Lifshitz theory of van der Waals interaction^{1,2} has previously been used to explain quantitatively the long-range attraction as two uncharged macroscopic surfaces approach one another across either air or water.^{3–7} It has also had reasonable success in explaining the spreading behavior of liquid alkanes on water^{8,9} and the surface tensions of liquid alkanes.^{9,10}

In this work, we use the Lifshitz theory of van der Waals interaction^{1,2} to calculate the contact angles of dispersive liquids on dispersive polymer surfaces. We follow closely the methodology that Hough and White have employed to calculate the contact angles of *n*-alkanes on poly(tetrafluoroethylene) (PTFE).⁹ The dispersive polymers are poly(dimethylsiloxane) (PDMS), poly(4-methyl-1-pentene) (TPX), polyethylene (PE), natural rubber (which is at least 97% *cis*-1,4-polyisoprene), and polystyrene (PS).

The dispersive liquids are diiodomethane, 1-bromonaphthalene, 1-methylnaphthalene, bromobenzene, *tert*-butylnaphthalene, liquid paraffin, and hexadecane. These liquids are frequently used as diagnostic liquids in studies aimed at obtaining information about polymer surface free energies. The structures of the five polymers are such that their interaction with the dispersive liquids should be dominated by van der Waals interactions (acid–base interactions should be unimportant) and there should be negligible complication due to specific orientation of polymer constituent groups at either the solid–vapor or solid–liquid interfaces. Previous experimental measurements provide values for the surface free energies and some contact angles of dispersive liquids on these polymer surfaces.^{7,9,11–26}

* To whom correspondence should be addressed.

[†] CSIRO Division of Chemicals and Polymers.

[‡] The University of Melbourne.

[Ⓢ] Abstract published in *Advance ACS Abstracts*, June 15, 1997.

- (1) Lifshitz, E. M. *J. Exp. Theor. Phys. USSR* **1955**, *29*, 94; *Sov. Phys. JETP* **1956**, *2*, 73.
- (2) Dzyaloshinskii, I. E.; Lifshitz, E. M.; Pitaevskii, L. P. *Adv. Phys.* **1961**, *10*, 165.
- (3) Israelachvili, J. N.; Tabor, D. *Proc. R. Soc. London, Ser. A* **1972**, *331*, 19.
- (4) Larson, I.; Drummond, C. J.; Chan, D. Y. C.; Grieser, F. *J. Am. Chem. Soc.* **1993**, *115*, 11885.
- (5) Biggs, S.; Mulvaney, P. *J. Chem. Phys.* **1994**, *100*, 8501.
- (6) Senden, T. J.; Drummond, C. J. *Colloid Surf. A* **1995**, *94*, 29.
- (7) Drummond, C. J.; Georgaklis, G.; Chan, D. Y. C. *Langmuir* **1996**, *12*, 2617.
- (8) Richmond, P.; Ninham, B. W.; Ottewill, R. H. *J. Colloid Interface Sci.* **1973**, *45*, 69.
- (9) Hough, D. B.; White, L. R. *Adv. Colloid Interface Sci.* **1980**, *14*, 3.
- (10) Israelachvili, J. N. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1729.

- (11) Chaudhury, M. K.; Whitesides, G. M. *Langmuir* **1991**, *7*, 1013.
- (12) Mangipudi, V.; Tirrell, M.; Pocius, A. V. *J. Adhes. Sci. Technol.* **1994**, *8*, 1251.
- (13) Mangipudi, V.; Tirrell, M.; Pocius, A. V. *Macromolecules* in press.
- (14) Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London, Ser. A* **1971**, *324*, 301.
- (15) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1981.
- (16) Arrowsmith, G. B.; Jeffrey, G. H.; Vogel, A. I. *J. Chem. Soc.* **1965**, 2072.
- (17) Baier, R. E.; Meyer, A. E. *Biofouling* **1992**, *6*, 165.
- (18) Bowers, R. C.; Zisman, W. A. In *Engineering Design for Plastics*; Baer, E., ed.; Van Nostrand Reinhold Co.: New York, 1964; Chapter 10.
- (19) Mangipudi, V. S. *Intrinsic Adhesion Between Polymer Films: Measurement of Surface and Interfacial Energies*, Ph.D. Thesis, University of Minnesota, 1995.
- (20) Owens, D. K.; Wendt, R. C. *J. Appl. Polym. Sci.* **1969**, *13*, 1741.
- (21) Dann, J. R. *J. Colloid Interface Sci.* **1970**, *32*, 302.
- (22) Kaelble, D. H.; Cirlin, E. H. *J. Polym. Sci.: Part A-2* **1971**, *9*, 363.
- (23) Fox, H. W.; Zisman, W. A. *J. Colloid Sci.* **1952**, *7*, 428.
- (24) Petke, F. D.; Ray, B. R. *J. Colloid Interface Sci.* **1969**, *31*, 216.
- (25) Fowkes, F. M.; McCarthy, D. C.; Mostafa, M. A. *J. Colloid Interface Sci.* **1980**, *78*, 200.
- (26) Ellison, A. H.; Zisman, W. A. *J. Phys. Chem.* **1954**, *58*, 503.

We also revisit the earlier treatment of the contact angles of *n*-alkanes on PTFE.⁹

Theoretical Considerations

Hough and White⁹ have provided a comprehensive description of the approach that we have taken in using the Lifshitz theory of van der Waals interaction to calculate the contact angles of dispersive liquids on dispersive polymers. Therefore, in this section we only provide a summary of the derivation of the most important relationships.

In order to calculate the contact angle (θ) of a dispersive liquid on a dispersive polymer surface, Young's equation is employed^{27,28}

$$\cos \theta = (\gamma_{PV} - \gamma_{PL})/\gamma_{LV} \quad (1)$$

where γ_{PV} , γ_{PL} , and γ_{LV} denote the polymer–vapor, polymer–liquid, and liquid–vapor surface free energy per unit area, respectively. It can also be shown that for dispersive materials⁹

$$\gamma_{PL} = \gamma_{PV} + \gamma_{LV} + E_{PVL} \quad (2)$$

so that

$$\cos \theta = \frac{-E_{PVL}}{\gamma_{LV}} - 1 \quad (3)$$

with

$$E_{PVL} = \frac{-A_{PVL}}{12\pi H_{0PVL}^2} \quad (4)$$

and

$$\gamma_{LV} = \frac{A_{LVL}}{24\pi H_{0LVL}^2} \quad (5)$$

where E_{PVL} is the van der Waals interaction free energy (per unit area) between polymer and liquid at equilibrium “contact” separation H_0 where the intervening medium is vacuum (or air), A_{PVL} is the associated nonretarded Hamaker constant for the heterointeraction between polymer and liquid across vacuum, and A_{LVL} is the nonretarded Hamaker constant for the homointeraction of the dispersive liquid across a vacuum. Therefore

$$\cos \theta = \frac{2A_{PVL}(H_{0LVL})^2}{A_{LVL}(H_{0PVL})^2} - 1 \quad (6)$$

This equation has been used to calculate the contact angles of the dispersive liquids on the dispersive polymer surfaces. The two nonretarded Hamaker constants were calculated from Lifshitz theory. The use of eq 6 also requires values to be given to the “contact” separations H_{0LVL} and H_{0PVL} . Contact angles were calculated by using four different approaches to obtain the ratio H_{0LVL}/H_{0PVL} . The first approach is the one which was used by Hough and White⁹ and assumes that $H_{0PVL} = H_{0LVL}$. The second approach assumes that $H_{0PVL} = H_{0PVP}$. The third and fourth approaches assume, respectively, a geometric mean relationship so that $H_{0PVL} = (H_{0PVP}H_{0LVL})^{1/2}$ and an arithmetic mean relationship so that $H_{0PVL} = (H_{0PVP} + H_{0LVL})/2$. H_{0LVL} is calculated from eq 5 and H_{0PVP} is defined

in terms of the surface free energy of a dispersive polymer, γ_{PV} , and can be calculated from

$$\gamma_{PV} = \frac{A_{PVP}}{24\pi H_{0PVP}^2} \quad (7)$$

where A_{PVP} is the nonretarded Hamaker constant for the homointeraction of the dispersive polymer across a vacuum.

The use of an arithmetic mean $H_{0PVL} = (H_{0PVP} + H_{0LVL})/2$ follows from extending the argument for ascribing H_{0PVP} and H_{0LVL} for pure substances as minimum cutoff separations between molecular layers in the respective bulk materials. The creation of a free surface is interpreted as the work done against van der Waals forces to split a bulk phase to form two free surfaces. For a heterointeraction the appropriate cutoff separation is simply taken as the arithmetic mean of the cutoff separations for the pure components.

The use of a geometric mean $H_{0PVL} = (H_{0PVP}H_{0LVL})^{1/2}$ follows from London dispersion theory where pairwise additivity of molecular interactions and identical electronic absorption band locations, ω_{UV} , for the polymer and liquid are assumed.^{29–34} The real situation of many-body interactions in condensed media means that, for bulk materials with similar ω_{UV} , the geometric mean relationship is not rigorously derived and should be viewed only as a first-order approximation.^{31,34}

The nonretarded Hamaker constants are governed by the dielectric properties of the interacting dispersive materials. Lifshitz theory was employed to determine the nonretarded Hamaker constants.^{1,2} The Ninham–Parsegian representation³⁵ of the dielectric permeability as a function of imaginary frequency ξ was used with

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

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

where ϵ_0 is the static dielectric constant, C_{IR} and C_{UV} are related to the oscillator strengths of the absorption bands in the infrared (IR) and ultraviolet (UV) regions, and ω_{IR} and ω_{UV} are the frequencies of the absorption band maxima.

The C_{UV} and ω_{UV} values for the polymers and liquids were determined from “Cauchy plots” of refractive index data from the low-frequency side of the ultraviolet absorption where the extinction coefficient is negligible (i.e., plots of $n^2 - 1$ versus $(n^2 - 1)\omega^2$, where the axis of ordinates intercept gives C_{UV} and the gradient gives $1/\omega_{UV}^2$). It was assumed that

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

where C_{MW} is related to the oscillator strengths of the absorption bands in the microwave (MW) region. For materials that have significant absorption in the microwave, i.e., diiodomethane, 1-bromonaphthalene, and bromobenzene, C_{MW} values were obtained from ref 36. These

(29) Girafalco, L. A.; Good, R. J. *J. Phys. Chem.* **1957**, *61*, 904.

(30) Good, R. J.; Girafalco, L. A. *J. Phys. Chem.* **1960**, *64*, 561.

(31) Fowkes, F. M. *Ind. Eng. Chem.* **1964**, *56*, 40.

(32) Good, R. J.; Hope, C. J. *J. Chem. Phys.* **1970**, *53*, 540.

(33) Good, R. J.; Hope, C. J. *J. Chem. Phys.* **1971**, *55*, 111.

(34) Tabor, D. In *Colloidal Dispersions*; Goodwin, J. W., Ed., Special Publication No. 43, The Royal Society of Chemistry: London, 1982; Chapter 2.

(35) Ninham, B. W.; Parsegian, V. A. *Biophys. J.* **1970**, *10*, 646.

(27) Young, T. *Philos. Trans. R. Soc. London* **1805**, *95*, 65.

(28) Bangham, D. H.; Razouk, R. I. *Trans. Faraday Soc.* **1937**, *33*, 1459.

Table 1. Physicochemical Properties of Dispersive Polymers at 20 °C

property	PDMS	TPX	PE	rubber	PS		PTFE.LD	PTFE.HD
					TE	TM		
ρ (g cm ⁻³)	1.0	0.83	0.915	0.906	1.059	1.059	2.1	2.3
ϵ_0	2.75	2.12	2.26	2.35	2.55	2.55	2.0	2.1
n_D	1.4127	1.467	1.482	1.5191	1.5882	1.5919	1.3434	1.3801
C_{UV}	0.961	1.114	1.146	1.250	1.440	1.451	0.792	0.890
$10^{-16}\omega_{UV}$ (rad s ⁻¹)	1.698	1.766	1.576	1.519	1.373	1.376	2.654	2.640
C_{IR}	0.789	0.01	0.114	0.10	0.110	0.100	0.21	0.21
$10^{-14}\omega_{IR}$ (rad s ⁻¹)	2.026	5.540	5.540	5.540	5.540	5.540	2.356	2.356
$10^{20}A_{PVP}$ (J)	4.4 ₃	5.6 ₄	5.2 ₈	5.7 ₆	6.3 ₆	6.4 ₄	5.0 ₅	6.0 ₂
γ_{PV} (mN/m)	21.8 ± 0.8	26.5 ± 2	33.3 ± 1.6	35 ± 2	44 ± 2	44 ± 2	>22.9	>27.3
H_{oPVP} (nm)	0.164 ± 0.003	0.168 ± 0.007	0.145 ± 0.004	0.148 ± 0.004	0.139 ± 0.003	0.139 ± 0.004	<0.171	<0.171

Table 2. Physicochemical Properties of Dispersive Liquids at 20 °C

property	diiodomethane		bromonaphthalene		methylnaphthalene	bromobenzene	<i>tert</i> -butylnaphthalene		hexadecane
	paraffin	liq	paraffin	liq			paraffin	liq	
ρ (g cm ⁻³)	3.201	3.201	1.4835	1.4835	1.0221	1.4914	0.9683	—	0.7733
ϵ_0	5.32	5.32	4.9	4.9	2.65	5.4	2.53	2.17	2.05
n_D	1.7411	1.7417	1.6580	1.6582	1.6180	1.5598	1.5800	1.4753	1.4347
C_{UV}	1.857	1.883	1.599	1.593	1.483	1.348	1.388	1.141	1.026
$10^{-16}\omega_{UV}$ (rad s ⁻¹)	1.088	1.161	1.090	1.070	1.105	1.3128	1.184	1.823	1.848
C_{IR}	0.2	0.2	0.151	0.157	0.17	0.11	0.14	0.030	0.025
$10^{-14}\omega_{IR}$ (rad s ⁻¹)	5.540	5.540	5.540	5.540	5.540	5.540	5.540	5.540	5.540
$10^{20}A_{LVL}$ (J)	7.1 ₉	7.8 ₀	5.9 ₂	5.7 ₉	5.3 ₆	5.6 ₅	5.2 ₃	6.0 ₃	5.2 ₃
γ_{LV} (mN/m)	50.8	50.8	44.44	44.44	39.80	36.34	33.7	32.4	27.47
H_{oLVL} (nm)	0.137	0.143	0.133	0.132	0.134	0.143	0.143	0.157	0.159

MW bands do not contribute significantly to the van der Waals interaction and a MW term does not need to be incorporated explicitly into the dielectric permeability function, eq 8.

Results and Discussion

The relevant physicochemical properties for the dispersive polymers and liquids examined in this work are summarized in Tables 1 and 2. The densities, dielectric constants, optical dispersion, location of the principal IR absorption bands, and surface free energies were obtained from a range of literature sources.^{7,9,11–19,36–48} The optical dispersion data for polystyrene⁴⁵ refers to a birefringent sample and we analyzed separately the transverse electric (TE; n_t) and transverse magnetic (TM; n_m) modes (Table 1). The surface free energies of PDMS, TPX, PE, natural rubber, and PS were obtained directly by measuring the adhesion between two homosurfaces (γ_{PV} equals half the

work of adhesion).^{11–14} The low-density (LD) and high-density (HD) PTFE surface free energies are lower boundaries which have been determined from an analysis of the dielectric properties and surface free energies of a wide range of perfluorocarbon materials.⁷ Some of the optical dispersion data from literature sources were sufficiently different to warrant separate analyses, and this is the reason for the two entries for both diiodomethane^{46,47} and 1-bromonaphthalene^{16,47} in Table 2. We could not find optical dispersion data for 1-*tert*-butylnaphthalene. Nevertheless, the (1-) and (2-) isomers have very similar n_D values, and therefore should exhibit similar dispersion behavior, so in this case we used the optical dispersion data for 2-*tert*-butylnaphthalene.¹⁶ Nonretarded Hamaker constants, determined with the data for the dielectric permeability function, and the H_o values, obtained from eq 7 for the polymers and eq 5 for the liquids, are also listed in Tables 1 and 2.

Israelachvili¹⁰ and Hough and White⁹ have shown for simple alkane liquids that H_{oLVL} correlates inversely with the square root of the liquid mass density, i.e., $H_{oLVL} \approx \rho^{-1/2}$. For the dispersive liquids and polymers studied in this work there is no apparent link between H_o and density (Tables 1 and 2). The lack of a correlation may be associated with the widely varying molecular geometry of the dispersive materials examined.

Equation 6 was employed to calculate Lifshitz theoretical contact angles. Tables 3–8 list the calculated contact angles and some experimental contact angles which were obtained from the literature.

Given that (i) we have used simple representations for the dielectric permeability functions of the polymers and liquids and (ii) the magnitude of experimental contact angles can depend on surface roughness, the size of the drop, the nature of the surrounding vapor, and the degree of purity of both the solid and liquid,⁴⁹ there is reasonable agreement between the calculated and experimental contact angles for the systems investigated. In general, the use of the arithmetic or geometric mean to estimate H_{oPVL} yielded very similar values, and both give better

(36) Buckley, F.; Maryott, A. A. Tables of Dielectric Dispersion Data for Pure Liquids and Dilute Solutions. *Natl. Bur. Stand. Circ.* **1958**, No. 589.

(37) Mills, N. J. In *Polymer Science—A Materials Science Handbook Vol. 1*; Jenkins, A. D., ed.; North-Holland Publishing Co.: Amsterdam, 1972; Chapter 7.

(38) Roff, W. J.; Scott, J. R. in *Fibres, Films, Plastics and Rubbers: A Handbook of Common Polymers*; Butterworths: London, 1971.

(39) Dörmann, H. In *Plastics for Engineers: Materials, Properties and Applications*, 3rd ed.; Hanser: Munich, 1993.

(40) Litman, A. M.; Fowler, N. E. In *Engineered Materials Handbook, Vol. 2: Engineering Plastics*; ASM International: Metals Park, OH, 1988; pp 460–478.

(41) Cooper, P. R. *Appl. Opt.* **1982**, 21, 3413.

(42) Wolpert, H. D. In *Engineered Materials Handbook, Vol. 2: Engineering Plastics*; ASM International: Metals Park, OH, 1988; pp 481–486.

(43) Newman, S. B. In *Analytical Chemistry of Polymers Part III. Identification Procedures and Chemical Analysis*; Kline, G. M., Ed.; Interscience: New York, 1962; p 283.

(44) Ashok, J.; Varaprasad, P. L. H.; Birch, J. R. in *Handbook of Optical Constants of Solids II*; Palik, E., Ed.; Academic Press, Inc.: New York, 1991; pp 957–987.

(45) Swalen, J. D.; Santo, R.; Tacke, M.; Fischer, J. *IBM J. Res. Dev.* **1977**, 21, 168.

(46) Vogel, A. I. *J. Chem. Soc.* **1948**, 1833.

(47) Gray, D. E., Ed. *American Institute of Physics Handbook*, 2nd ed.; McGraw-Hill: New York, 1963; pp 6–90.

(48) Partington, J. R. *An Advanced Treatise on Physical Chemistry, Vol. 4. Physico-Chemical Optics*; Longmans: London, 1953; pp 52–53.

(49) Yekta-Fard, M.; Ponter, A. B. *J. Adhes. Sci. Technol.* **1992**, 6, 253.

Table 3. Nonretarded Hamaker Constants and Contact Angles for Dispersive Liquids on Poly(dimethylsiloxane) (PDMS)

liquid	Hamaker constants $10^{20}A_{LVL}$ (J) $10^{20}A_{PVL}$ (J)		contact angles (deg)				
			theoretical				experimental θ_A (θ_R)
			$H_{oPVL} = H_{oLVL}$	$H_{oPVL} = H_{oPVP}$	$H_{oPVL} = (H_{oPVP}H_{oLVL})^{1/2}$	$H_{oPVL} = (H_{oPVP} + H_{oLVL})/2$	
diiodomethane	7.18 ₈ ; 7.79 ₉	5.57 ₄ ; 5.83 ₃	57; 60	85; 82	73; 72	74; 73	70 (70); ¹¹ 70; ¹⁸ 71 ± 5 ¹⁷
bromonaphthalene	5.93 ₀ ; 5.79 ₅	5.05 ₁ ; 4.98 ₅	45; 44	83; 83	68; 67	69; 68	56; ¹⁸ 62 ± 3 ¹⁷
methylnaphthalene	5.35 ₈	4.80 ₃	38	77	62	63	52 ± 3 ¹⁷
bromobenzene	5.63 ₁	4.96 ₉	40	70	57	59	
<i>tert</i> -butylnaphthalene	5.23 ₀	4.76 ₅	35	67	54	55	49 ¹⁸
liq paraffin	6.03 ₄	5.15 ₉	45	55	50	51	51 (40) ¹¹
hexadecane	5.22 ₃	4.80 ₁	33	43	39	40	36; ¹⁸ 39 ± 4; ¹⁷ 40 (26) ¹¹

Table 4. Nonretarded Hamaker Constants and Contact Angles for Dispersive Liquids on Poly(4-methyl-1-pentene) (TPX)

liquid	Hamaker constants $10^{20}A_{LVL}$ (J) $10^{20}A_{PVL}$ (J)		contact angles (deg)				
			theoretical				experimental θ_A (θ_R)
			$H_{oPVL} = H_{oLVL}$	$H_{oPVL} = H_{oPVP}$	$H_{oPVL} = (H_{oPVP}H_{oLVL})^{1/2}$	$H_{oPVL} = (H_{oPVP} + H_{oLVL})/2$	
diiodomethane	7.18 ₈ ; 7.79 ₉	6.23 ₄ ; 6.53 ₄	43; 47	81; 78	66; 65	66; 65	67 (67) ¹⁹
bromonaphthalene	5.93 ₀ ; 5.79 ₅	5.64 ₃ ; 5.56 ₆	25; 23	79; 79	60; 59	61; 61	61 (61) ¹⁹
methylnaphthalene	5.35 ₈	5.37 ₅	spreads	74	53	55	
bromobenzene	5.63 ₁	5.56 ₇	12	64	47	48	
<i>tert</i> -butylnaphthalene	5.23 ₀	5.34 ₀	spreads	61	42	43	
liq paraffin	6.03 ₄	5.83 ₁	21	47	36	36	
hexadecane	5.22 ₃	5.42 ₅	spreads	31	15	15	

Table 5. Nonretarded Hamaker Constants and Contact Angles for Dispersive Liquids on Poly(ethylene) (PE)

liquid	Hamaker constants $10^{20}A_{LVL}$ (J) $10^{20}A_{PVL}$ (J)		contact angles (deg)				
			theoretical				experimental θ_A (θ_R)
			$H_{oPVL} = H_{oLVL}$	$H_{oPVL} = H_{oPVP}$	$H_{oPVL} = (H_{oPVP}H_{oLVL})^{1/2}$	$H_{oPVL} = (H_{oPVP} + H_{oLVL})/2$	
diiodomethane	7.18 ₈ ; 7.79 ₉	6.09 ₃ ; 6.37 ₃	46; 51	59; 54	53; 52	53; 52	46 ± 3; ²¹ 50 (49); ¹⁹ 51 ± 2; ¹⁷ 51.9 ± 0.5; ²⁵ 52 ± 2; ²³ 53; ²⁰ 55 ²²
bromonaphthalene	5.93 ₀ ; 5.79 ₅	5.52 ₀ ; 5.44 ₈	30; 28	56; 56	45; 45	45; 45	33 ± 3; ²¹ 35 (7); ²⁴ 35 ± 2; ²³ 36 ± 2; ¹⁷ 40 (36); ¹⁹ 41 ²²
methylnaphthalene	5.35 ₈	5.25 ₆	16	48	36	36	27 ± 4 ¹⁷
bromobenzene	5.63 ₁	5.42 ₂	22	29	26	26	13 ²⁴
<i>tert</i> -butylnaphthalene	5.23 ₀	5.21 ₃	7	20	15	15	7 ± 2 ²³
liq paraffin	6.03 ₄	5.62 ₈	30	spreads	spreads	spreads	
hexadecane	5.22 ₃	5.23 ₇	spreads	spreads	spreads	spreads	spreads ^{17,22,23}

Table 6. Nonretarded Hamaker Constants and Contact Angles for Dispersive Liquids on Natural Rubber

liquid	Hamaker constants $10^{20}A_{LVL}$ (J) $10^{20}A_{PVL}$ (J)		contact angles (deg)				
			theoretical				experimental θ_A (θ_R)
			$H_{oPVL} = H_{oLVL}$	$H_{oPVL} = H_{oPVP}$	$H_{oPVL} = (H_{oPVP}H_{oLVL})^{1/2}$	$H_{oPVL} = (H_{oPVP} + H_{oLVL})/2$	
diiodomethane	7.18 ₈ ; 7.79 ₉	6.37 ₆ ; 6.66 ₇	39; 45	59; 53	50; 49	50; 49	
bromonaphthalene	5.93 ₀ ; 5.79 ₅	5.77 ₆ ; 5.70 ₂	19; 15	55; 56	41; 41	42; 41	
methylnaphthalene	5.35 ₈	5.50 ₁	spreads	47	31	31	
bromobenzene	5.63 ₁	5.67 ₀	spreads	28	19	19	
<i>tert</i> -butylnaphthalene	5.23 ₀	5.45 ₄	spreads	19	spreads	spreads	
liq paraffin	6.03 ₄	5.87 ₆	19	spreads	spreads	spreads	
hexadecane	5.22 ₃	5.46 ₈	spreads	spreads	spreads	spreads	

agreement between theory and experiment than the assumption $H_{oLVL} = H_{oPVL}$ used earlier.⁹

Hough and White used the approach outlined in this work, with $H_{oLVL}/H_{oPVL} = 1$, to examine the contact angles of *n*-alkanes on PTFE.⁹ It has recently been suggested that the data used to construct the UV part of their dielectric representation for PTFE was incorrect.⁷ Therefore we re-examined the PTFE system with what is believed by us to be a more precise representation of the dielectric permeability function (Table 1). We were not sure whether the PTFE surface that was employed in the experimental investigation was low-density (LD), high-density (HD), or some intermediate density PTFE. There-

fore, we performed two sets of calculations, one set based on the assumption that the surface was PTFE.LD and the other set assuming that it was PTFE.HD, which provide the boundaries that should contain the actual PTFE. The dielectric representations for the *n*-alkanes were taken from the review of Hough and White.⁹ Using any of the four approaches to obtain H_{oPVL} results in poor agreement between calculated and experimental contact angles. We have found that, in general, a H_{oPVL} greater than either H_{oLVL} or H_{oPVP} is required in order to obtain agreement between the theoretical and the experimental contact angles (Table 9). This finding may be partly, but not entirely, associated with the fact that perfluorocarbons

Table 7. Nonretarded Hamaker Constants and Contact Angles for Dispersive Liquids on Poly(styrene) TE (PS TE)

liquid	Hamaker constants		contact angles (deg)				experimental θ_A (θ_R)
	$10^{20}A_{LVL}$ (J)	$10^{20}A_{PVL}$ (J)	theoretical				
			$H_{oPVL} = H_{oLVL}$	$H_{oPVL} = H_{oPVP}$	$H_{oPVL} = (H_{oPVP}H_{oLVL})^{1/2}$	$H_{oPVL} = (H_{oPVP} + H_{oLVL})/2$	
diiodomethane	7.18 ₈ ; 7.79 ₉	6.72 ₇ ; 7.02 ₆	29; 37	35; 25	32; 31	32; 31	37 ± 3; ²¹ 35 ± 2; ²⁶ 31 (31) ¹⁹
bromonaphthalene	5.93 ₀ ; 5.79 ₅	6.09 ₈ ; 6.02 ₁	spreads	28; 29	15; 13	15; 14	14 ± 3; ²¹ 15 ± 2; ²⁶ 11 (11) ¹⁹
methylnaphthalene	5.35 ₈	5.80 ₇	spreads	spreads	spreads	spreads	
bromobenzene	5.63 ₁	5.96 ₉	spreads	spreads	spreads	spreads	
<i>tert</i> -butylnaphthalene	5.23 ₀	5.75 ₁	spreads	spreads	spreads	spreads	
liq paraffin	6.03 ₄	6.15 ₀	spreads	spreads	spreads	spreads	
hexadecane	5.22 ₃	5.72 ₃	spreads	spreads	spreads	spreads	

Table 8. Nonretarded Hamaker Constants and Contact Angles for Dispersive Liquids on Poly(styrene) TM (PS TM)

liquid	Hamaker constants		contact angles (deg)				experimental θ_A (θ_R)
	$10^{20}A_{LVL}$ (J)	$10^{20}A_{PVL}$ (J)	theoretical				
			$H_{oPVL} = H_{oLVL}$	$H_{oPVL} = H_{oPVP}$	$H_{oPVL} = (H_{oPVP}H_{oLVL})^{1/2}$	$H_{oPVL} = (H_{oPVP} + H_{oLVL})/2$	
diiodomethane	7.18 ₈ ; 7.79 ₉	6.76 ₆ ; 7.06 ₈	28; 36	34; 23	31; 30	31; 30	37 ± 3; ²¹ 35 ± 2; ²⁶ 31 (31) ¹⁹
bromonaphthalene	5.93 ₀ ; 5.79 ₅	6.13 ₄ ; 6.05 ₇	spreads	27; 28	12; 10	12; 14	14 ± 3; ²¹ 15 ± 2; ²⁶ 11 (11) ¹⁹
methylnaphthalene	5.35 ₈	5.84 ₀	spreads	spreads	spreads	spreads	
bromobenzene	5.63 ₁	6.00 ₄	spreads	spreads	spreads	spreads	
<i>tert</i> -butylnaphthalene	5.23 ₀	5.78 ₅	spreads	spreads	spreads	spreads	
liq paraffin	6.03 ₄	6.19 ₀	spreads	spreads	spreads	spreads	
hexadecane	5.22 ₃	5.75 ₉	spreads	spreads	spreads	spreads	

Table 9. Nonretarded Hamaker Constants and Equilibrium "Contact" Surface Separations for the PTFE-Alkane Systems^a

liquid	$10^{20}A_{LVL}$ (J)	H_{oLVL} (nm)	experimental θ_A	PTFE.LD		PTFE.HD	
				$10^{20}A_{PVL}$ (J)	H_{oPVL} (nm)	$10^{20}A_{PVL}$ (J)	H_{oPVL} (nm)
hexadecane	5.22 ₃	0.159	46	5.07 ₁	0.170	5.53 ₄	0.178
tetradecane	5.10 ₃	0.159	44	5.01 ₁	0.170	5.46 ₈	0.178
dodecane	5.03 ₄	0.162	45	4.98 ₂	0.173	5.43 ₇	0.181
undecane	4.88 ₀	0.162	39	4.89 ₉	0.172	5.34 ₇	0.180
decane	4.82 ₅	0.164	35	4.87 ₆	0.173	5.32 ₁	0.180
nonane	4.66 ₆	0.164	32	4.79 ₂	0.173	5.22 ₉	0.181
octane	4.49 ₈	0.166	26	4.70 ₃	0.174	5.13 ₂	0.182
heptane	4.31 ₄	0.169	21	4.60 ₆	0.177	5.02 ₆	0.185
hexane	4.07 ₁	0.172	12	4.47 ₂	0.180	4.88 ₀	0.189
pentane	3.75 ₂	0.176	spreads	4.29 ₂		4.68 ₃	

^a H_{oPVL} values have been calculated by using experimental advancing contact angles and eq 6.

have higher ω_{UV} values than hydrocarbons; e.g., compare the PTFE ω_{UV} in Table 1 with those of the hydrocarbon liquids in Table 2. This difference in the ω_{UV} values may also be a contributing factor to both the critical surface tensions, γ_c , obtained from Zisman plots (plots of $\cos \theta_A$ versus γ_{LV} , with the extrapolation of γ_{LV} to $\cos \theta_A = 1$ giving γ_c),⁵⁰ and the Good-Girafalco-Fowkes relationship, $\gamma_{GGF} = \gamma_{LV}((\cos \theta + 1)/2)^2$,²⁹⁻³¹ providing underestimates of the actual surface free energies of perfluorocarbon solids when hydrocarbons are employed as the diagnostic liquids.⁷ This situation was recognized by Fowkes over 30 years ago but is frequently ignored.³¹

Conclusions

The Lifshitz theory of van der Waals interaction has been used to calculate the change in interfacial energy (the term E_{PVL} in eq 3) when a liquid-vapor and a polymer-vapor interface are brought together to form a polymer-liquid interface. Since only dispersion interac-

tions are involved in the polymer-liquid systems that we have considered, one would expect Lifshitz theory to be able to predict the correct trend across a family of similar compounds. Being a theory based on interacting macroscopic continua, one would expect the need to provide a cutoff separation, H_{oPVL} , for the theory. For the silicone-hydrocarbon and hydrocarbon-hydrocarbon systems investigated, H_{oPVL} values determined by applying either the geometric mean or arithmetic mean relationships provide theoretical contact angles that are in reasonable agreement with experimentally measured contact angles. The fact that the required H_{oPVL} values are insensitive to how they are calculated lends support to the use of the continuum Lifshitz approach. The results of this investigation support the contention that for van der Waals interaction in silicone-hydrocarbon and hydrocarbon-hydrocarbon systems the geometric mean relationship, that is frequently employed to relate surface free energies and contact angles, is a reasonable first-order approximation. On the other hand, for perfluorocarbon-hydrocarbon interaction the indications are that the simple geometric

mean relationship is a poor approximation. For the PTFE-alkane systems, irrespective of the approach taken to estimate H_{OPVL} , the calculated contact angles are less than the experimentally measured contact angles. At this stage, we are unable to explain completely this finding. Nevertheless, we speculate that it may be associated with the calculated value for γ_{PL} being too large or, in other words, Lifshitz theory providing a poor estimate of the term E_{PVL} in eq 3. This possibility can be investigated further by experimental measurement of both the pull-off forces (work of adhesion) and surface force-separation

curves (van der Waals force profile; Hamaker function) associated with perfluorocarbon-hydrocarbon interactions in air.^{7,12,13}

Acknowledgment. We thank both Mr. Darrell Wells (CSIRO) and Mr. George Georgaklis (CSIRO) for help in manuscript preparation. We also thank Professor Matt Tirrell (University of Minnesota) for supplying preprints of some of his work.

LA962131C