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Prediction of static contact angles on the basis of molecular forces and adsorption data

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At a three-phase contact line, a liquid bulk phase is in contact with and coexists with a very thin layer of adsorbed molecules. This adsorbed film in the immediate vicinity of a liquid wedge modifies the balance of forces between the liquid and solid phases such that, when included in the balance of forces, a quantitative relationship emerges between the adsorbed film thickness and the static contact angle. This relationship permits the prediction of static contact angles from molecular forces and equilibrium adsorption data by means of quantities that are physically meaningful and measurable. For *n*-alkanes on polytetrafluoroethylene, for which there are experimental data available on adsorption and contact angles, our computations show remarkable agreement with the data. The results obtained are an improvement on previously published calculations—particularly for alkanes with a low number of carbon atoms, for which adsorption is significant.

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I. INTRODUCTION

Contact angles play an essential role in many industrial processes such as coating, painting, cleaning, printing, oil recovery, etc. Even so, the theoretical prediction of contact angles remains an unresolved problem. The traditional way of calculating contact angles follows Young's equation [1] that describes the static contact angle, θ_o, as a balance of forces at the three-phase contact line due to the interfacial tensions at the vapor-liquid, σ, solid-vapor, σ_{SV}, and solid-liquid, σ_{SL}, interfaces (Table I). Doubts about the validity of Young's equation arose with the derivation of alternative equations for the contact angle based on intermolecular forces. The equations obtained on this basis, using a variety of approaches, are shown in Table I. Miller and Ruckenstein [2] and Jameson and del Cerro [3] developed equivalent equations for the contact angle as a function of the Hamaker constants, A_{SL} and A_{LL}, based on different arguments. Jameson and del Cerro incorrectly assumed their result to be an expression for the equilibrium contact angle. However, it actually describes the mechanical equilibrium of a liquid wedge, of constant angle of inclination, and the macroscopic contact angle computed using their equation is in fact the advancing contact angle [4]. Hough and White [5] derived a simple equation for the contact angle (Table I) also in terms of Hamaker constants and tested its validity with alkanes on polytetrafluoroethylene (PTFE). Their prediction of contact angles, of large alkane carbon number, is excellent but it failed for alkanes with low carbon number. Churaev [6] developed an equation for the contact angle (Table I) in terms of a length (h_o) that is a film thickness "on the order of molecular size—such as the thickness of adsorbed layers" and proceeded to simplify it to obtain an equation equivalent to that of Hough and White [5] assuming equality of h_o for both liquid-liquid and liquid-solid interactions. Drummond *et al.* [7] used an equivalent approach to that of Hough and White [5] to explore three more equations based on potential relationships between "contact" separations. Their results were, in fact, unsatisfactory for the PTFE-alkane systems. Wayner [8] obtained an equation for the contact angle as a function of an "effective film thickness at the contact line," δ_0, and a parameter, a, calculated from interfacial surface tensions and Hamaker constants. He compared experimental contact angles again for *n*-alkanes on PTFE and obtained satisfactory predictions for contact angle values $\leqslant 26^\circ$. More recently, Slattery *et al.* [9] developed a theory based on a jump momentum balance at the interface by considering molecular forces and Young's equation. They validated the equation by predicting contact angles for the *n*-alkanes on PTFE and various dispersive liquids on polydimethylsiloxane but did not show results for small contact angles (*n*-hexane on PTFE).

Despite recognizing the role of adsorbed films on static contact angles, none of these research endeavors provided a quantitative, predictive theory relating static contact angles to adsorption phenomena. The theories presented in Table I either do not consider molecular forces [1] or assume a geometry for the molecular force formulation (a flat film [5–9]) or a wedge that extends down to the solid surface with a constant angle of inclination [2,3]) that does not include the presence of an adsorbed film. Additionally, none of these theories take account of the effect of the molecular forces on interfacial tension [10] and only constant bulk values (valid away from a dense third phase and from electrostatic and magnetic effects) are taken into account.

In a recent publication, Diaz *et al.* [4] modified the balance of forces at the gas-liquid interface to take into account the presence of an adsorbed film in the region adjacent to the three-phase contact line and included in the formulation the spatial variation of the gas-liquid interfacial free energy by integration of the disjoining or conjoining pressure [10]. The theoretical analysis performed by Diaz *et al.* [4] provided an explanation for a certain type of contact angle hysteresis due to the presence (receding) or absence (advancing) of the adsorbed film. In this paper it is shown how the equilibrium force balance relationship can be used to predict contact angles

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TABLE I. Comparison of the different approaches for the calculation of the macroscopic contact angle.

Assumptions	Authors	Mathematical expression for contact angle	Length definition
(1) Constant interfacial tensions (2) No molecular forces	Young [1]	$\sigma_{SV} = \sigma \cos\theta_o + \sigma_{SL}$	
(1) Constant interfacial tensions (2) Molecular forces included. Formulation of the molecular force balance: *for a flat film*	Miller and Ruckenstein [2], Jameson and del Cerro [3]	$\frac{1}{2} + \frac{3}{4}\cos\theta_o - \frac{1}{4}\cos^3\theta_o = \frac{A_{SL}}{A_{LL}}$	
	Hough and White [5]	$\cos\theta_o = 2\frac{A_{SL}}{A_{LL}} - 1$; $\cos\theta_o = \frac{A_{SL}}{12\pi\sigma L_C^2} - 1$	L_C: solid-liquid cutoff distance
	Wayner [8]	$\cos\theta_o = 1 - \frac{1}{3a\delta_0^2}$	δ_0: thickness is of molecular size
	Churaev [6]	$\cos\theta_o = 1 - \frac{A_{LL}-A_{SL}}{12\pi\sigma h_o^2}$	h_o: film thickness "on the order of molecular size, like the thickness of adsorbed layers"
		$\cos\theta_o = 2\frac{A_{SL}}{A_{LL}} - 1$	"Equality of h_o for liquid-liquid and liquid-solid interactions was assumed"
	Drummond [7]	$\cos\theta_o = 2\frac{A_{SL}}{A_{LL}}(\frac{H_{oLVL}}{H_{oPVL}})^2 - 1$	H_o: equilibrium "contact" separation
	Slattery [9]	$\cos\theta_o = \frac{\sigma_{SV}-\sigma_{SL}}{\sigma} - \frac{A_{LL}-A_{SL}}{12\pi\sigma\delta^{(SL)2}}$	$\delta^{(SL)}$: separation distance between phases *A* and *B*
(1) Variable interfacial tensions (2) Molecular forces included. Formulation of the molecular force balance:*for an adsorbed (flat) film in equilibrium with a wedge (inclined surface)*	Diaz *et al.* [4]	$\cos\theta_o = 1 + \ln\left[1 - \frac{A_{LL}-A_{SL}}{12\pi\sigma(D_{\text{ads}}+D_m)^2} - \frac{A_{LL}}{12\pi\sigma D_m^2}(-\frac{1}{2}+\frac{3}{4}\cos\theta_o - \frac{1}{4}\cos^3\theta_o)\right]$	D_{ads} : adsorption film thickness from adsorption isotherms. D_m : cutoff length

based on experimental adsorption data. By demonstrating the need to take into account the presence of an adsorbed film, this paper aims to advance two concepts: First, the thickness of the adsorbed film on a flat surface can be used to determine static contact angles and in turn static contact angles can be used to measure adsorbed film thickness. Second, the balance of forces, including molecular forces and the presence of an adsorbed film, should be the standard model for the description and prediction of static contact angles. This second concept should also help to render the use of Young's relationship—for the analysis of contact angle phenomena—as unnecessary.

II. MODEL FORMULATION

The analysis is restricted to a simple geometry, namely a two-dimensional fluid slice standing on top of a flat, horizontal surface in contact with a layer of an adsorbed film of liquid, of thickness D_{ads}, (Fig. 1). For this geometry, the mean curvature of the air-liquid interface is determined by the curvature on a plane normal to the solid plane. The second principal curvature, in a direction parallel to the plane of the solid surface, is assumed to be small and can be safely neglected.

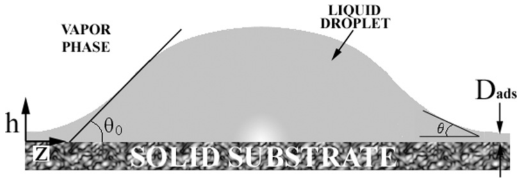

FIG. 1. Sketch of a bulk phase droplet coexisting with an adsorbed film of the same liquid.

The basic premises are as follows:

(1) The true shape of a vapor-liquid interface in the near vicinity of the contact line is accurately described by the fully augmented Young-Laplace (FAYL) equation—that takes into account capillary, gravity, and molecular forces represented by the disjoining pressure and the spatially varying interfacial free energy:

The FAYL is a natural extension of the known augmented Young-Laplace (AYL) equation where disjoining pressure (the term "disjoining" is used generically to include both disjoining and conjoining pressure) is included in the formulation of the pressure balanced by capillary forces. Also included in the FAYL is the effect of disjoining pressure on the gas-liquid interfacial tension. According to Derjaguin *et al.* [10], the spatial variation of the vapor-liquid free energy (g_{VL}) is given by

$$g_{VL}(h,\theta) = \sigma + \int_h^\infty \Pi(h,\theta)dh, \tag{1}$$

where h is the thickness of the liquid film, σ is the bulk value of the specific Gibbs free energy of the vapor-liquid interface and Π is the disjoining pressure. Within a close vicinity of the contact line (the molecular region), the pressure field due to gravity is essentially constant and negligible compared to that due to capillary and molecular forces, and the FAYL equation reduces to

$$g_{VL}(h,\theta)(2H) = \frac{dg_{VL}(h,\theta)}{dh}. \tag{2}$$

The left-hand side of Eq. (2) represents the capillary force with the interfacial free energy varying due to the effect of molecular forces [Eq. (1)]. The right-hand side of Eq. (2) represents the disjoining pressure obtained by differentiation of Eq. (1). Integration of Eq. (2) can be performed analytically using the definition of the mean curvature of the air-liquid interface ($2H = -\frac{d\cos\theta}{dh}$ [11]) and considering as limits of integration (i) a point on the outer edge of the molecular region where $g_{VL} = \sigma$ and $\theta = \theta_o$, and (ii) the horizontal adsorbed film where $\cos\theta = 1$ [4]:

$$\cos\theta_0 = 1 + \ln\left[1 + \frac{1}{\sigma}\int_{D_{\text{ads}}}^{\infty} \Pi(h,\theta)dh\right]. \tag{3}$$

This equation can be used for the theoretical prediction of contact angles, when the disjoining pressure function $\Pi(h,\theta)$, the bulk value of the interfacial free energy σ, and the adsorption film thickness D_{ads}, are known. If the AYL is integrated instead of the FAYL, a simpler form without the logarithm term is developed and an equation equivalent to the Frumkin-Derjaguin theory is obtained.

(2) The disjoining pressure function, $\Pi(h,\theta_o)$, must be reformulated to account for changes in the molecular force field due to the presence of an adsorbed film on the solid surface in contact with a bulk phase:

Because of the difficulties of integrating a complex functional over a curved surface as represented in Fig. 1, we assumed that the liquid phase has a wedgelike shape with a constant inclination angle θ_o and reformulated the simple wedge analyses previously performed [2,3], adding an adsorbed liquid film of thickness D_{ads} to the solid-vapor interface. The molecular force balance for this geometry leads to an analytical expression for the disjoining pressure near a contact line for nonpolar liquids [4]:

$$\Pi(h,\theta_o) = -\frac{A_{LL} - A_{SL}}{6\pi h^3} - \frac{A_{LL}}{12\pi(h - D_{\text{ads}})^3} \times\left[-1 + \frac{3}{2}\cos(\theta_o) - \frac{1}{2}\cos^3(\theta_o)\right]. \tag{4}$$

Equation (4) is the only available disjoining pressure function that describes the balance of forces on a molecule at a liquid-gas interface—for a flat drop of liquid sitting on a solid horizontal surface, when there is a film of adsorbed liquid at the edge of the three-phase contact line. Many previous works have recognized the need to take into account the effect of the adsorbed film on the balance of forces but none have introduced it in a quantitative way. Equation (4) can be easily simplified to the equation obtained by Miller and Ruckenstein [2] and later by Jameson and del Cerro [3], for a wedge in the absence of adsorption, by taking $D_{\text{ads}} = 0$.

Combination of Eqs. (3) and (4) leads to an expression that now relates contact angle to adsorption film thickness [4]:

$$\cos\theta_o = 1 + \ln\left[1 - \frac{A_{LL} - A_{SL}}{12\pi\sigma(D_{\text{ads}} + D_m)^2} - \frac{A_{LL}}{12\pi\sigma D_m^2} \times\left(-\frac{1}{2} + \frac{3}{4}\cos\theta_o - \frac{1}{4}\cos^3\theta_o\right)\right], \tag{5}$$

where D_m is a cutoff length needed to estimate the strength of binary molecular interactions. Equation (5) reflects the main premises used to derive it; (i) the logarithmic form of the equation is due to the effect of disjoining pressure on total pressure as well as on the local value of the interfacial tension, and (ii) the term involving D_{ads} (inside the brackets) reflects the effect of the adsorbed film on the computation of the disjoining pressure. Static contact angles and low Reynolds number dynamic contact angles, are shaped by molecular forces through the development of an additional pressure field due to attraction by the solid phase and the dampening effect of an adsorbed film on the solid surface.

All the physical parameters included in Eq. (5) have physical meaning and are capable of experimental measurement as shown in Sec. III. In fact, Eq. (5) and all similar equations with alternative expressions for the molecular forces constitute the most up to date equation(s) for the static contact angle θ_o.

III. RELATIONSHIP BETWEEN ADSORPTION AND CONTACT ANGLES

A. Parameters

With access to four constants: (1) the Hamaker constant for liquid-liquid interactions, (2) the Hamaker constant for the appropriate solid-liquid interactions, (3) the cutoff length for liquid molecules, and (4) the thickness of the adsorbed layer of liquid molecules on the solid surface adjacent to the molecular region of the triple phase contact line, one can compute *ab initio* values of the static contact angle by means of Eq. (5). Indeed these four constants are capable of direct or indirect experimental measurement but, unfortunately, there are not many systems where the complete set of parameters is available. The validity of Eq. (5) is tested by predicting contact angle values for *n*-alkanes on PTFE. Hamaker constants for the systems under study were computed from Lifshitz theory by Hough and White [5] and are reported in Table II. The available experimental thicknesses of the adsorbed submonolayer [12–14] are shown in Table II. Finally, the molecular cutoff diameters are estimated by means of Eq. (6), which has been obtained by comparing a simplified form of Eq. (5), resulting from a first order Taylor series approximation for the natural log, and the equation for the contact angle reported by Hough and White [5] in terms of A_{SL} (Table I):

$$\sigma = \frac{A_{LL}}{24\pi(D_{\text{ads}} + D_m)^2} + \frac{A_{LL}}{24\pi D_m^2} \times\left(-\frac{1}{2} + \frac{3}{4}\cos\theta_o - \frac{1}{4}\cos^3\theta_o\right). \tag{6}$$

Equation (6) reduces to the expression for interfacial tension of nonpolar liquids used by other authors (Padday and Uffindell [15], Israelachvili [16], Jameson and del Cerro [3], and Churaev [17]) for a bulk phase:

$$\sigma = \frac{A_{LL}}{24\pi D_o^2}. \tag{7}$$

Israelachvili [16] (p. 202) ponders on whether D_o should be the distance between two atomic centers but argues that

TABLE II. Experimental and calculated data for n-alkanes over polytetrafluoroethylene (PTFE).

	Experimental/calculated data					Contact angle prediction					Experimental contact angle
Number of carbon atoms	σ[a] (N/m)	A_{SL}[b] (10^{20} J)	A_{LL}[b] (10^{20} J)	D_{ads} (10^{11} m)	D_m[c] (10^{10} m)	θ_o[d] (deg)	θ_o[e] (deg)	θ_o[f] (deg)	θ_o[g] (deg)	θ_o[h] (deg)	θ_o[a] (deg)
6	0.0184	3.91	4.06	15.4[i]	0.15	spreads	21.6	11.5	(spreads)	10.6	12
8	0.0218	4.11	4.49	8.10[j]	0.81	32.6	33.5	26	28.2	27.1	26
10	0.0239	4.25	4.81	4.30[j]	1.17	40.6	39.8	39	35.5	34.3	35
12	0.0254	4.35	5.03		1.59	45.0	43.1	54	39.6	39.6	42
14	0.0267	4.38	5.09		1.56	48.3	44.1		43.3	40.2	44
16	0.0276	4.43	5.22		1.55	50.4	45.8	67	45.1	41.7	46

[a] Experimental values for interfacial tension, σ, and contact angles were determined by Fox and Zisman [19].

[b] Hamaker constants were determined by Hough and White [5].

[c] Cutoff lengths were computed by simultaneously solving Eqs. (5) and (6).

[d] Computed by Young's equation [1].

[e] Provided by Hough and White [5].

[f] Provided by Wayner [8].

[g] Provided by Slattery *et al.* [9]. θ_o is not available for hexane. In parentheses is the result obtained applying Slattery's model.

[h] Computed by simultaneously solving Eqs. (5) and (6).

[i] Adsorption film thickness was estimated from the adsorption data by Whalen [14].

[j] Adsorption film thickness was compiled by Adamson [12] from original data of Wade and Whalen [13].

this concept is compromised by the use of "smooth" surfaces in the computation of molecular forces and that D_o should be "substantially less" than the molecular distance. For Churaev [17] it is a film thickness "of the order of molecular size—such as the thickness of an adsorbed layer." In general, D_m (or D_o) is a "cutoff" length that depends on the molecular force model used and on the relative packing of different molecular species.

B. Contact angle prediction

For the systems under study, D_m and θ_o are obtained by simultaneously solving Eqs. (5) and (6). As D_{ads} is only available for the alkanes with a low number of carbon atoms—and considering that its value (compared to D_m) is decreasingly significant as volatility decreases (for example, for decane, D_{ads} is one order of magnitude smaller than D_m), we assume $D_{\mathrm{ads}} \approx 0$ for high carbon numbers. Table II shows the computed values of D_m and θ_o. In a previous paper [4], use is made of a constant cutoff length and D_{ads} is calculated using Eq. (5). In this study, the development of Eq. (6) and the consideration of experimental data [12–14] on adsorption isotherms permits the calculation of D_m and θ_o with no adjustable parameters; furthermore, the parameters included in our model, σ, $A_{LL}^{[6]}$, $A_{SL}^{[6]}$, and D_{ads}, are physically meaningful, measurable quantities. Figure 2 compares experimental contact angle data with theoretical values predicted by several authors, including this work. The contact angles predicted using Eq. (5) are remarkably close to the experimental values considering the diverse sources of experimental and computed data. For alkanes with a low number of carbon atoms, for which adsorption is significant, the theoretical prediction of the contact angle improves previous analyses. For alkanes with a higher number of carbon atoms, the models by Hough and White [5] and by Slattery *et al.* [9] provide better consistency with experimental data. This is probably due to the low adsorption of these systems that has been modeled by means of a theory that assumes adsorption to be significant for the prediction of contact angles and was developed for a wedge in equilibrium with an adsorbed film of thickness D_{ads}. According to the results shown in Table II and Fig. 2, the theoretical prediction of contact angles using Eqs. (5) and (6) provides improved or satisfactory results for contact angles up to around 40°, being those systems that have lower surface tension and are more volatile.

Figure 3 shows a graphical representation of molecular cutoff lengths, D_m, and of adsorbed film thickness, D_{ads}, against the number of carbon atoms of the hydrocarbon chain. Considering that cutoff length should be a function of solid surface roughness and liquid molecular size, as expected, D_m increases with the number of carbon atoms of the hydrocarbon chain.

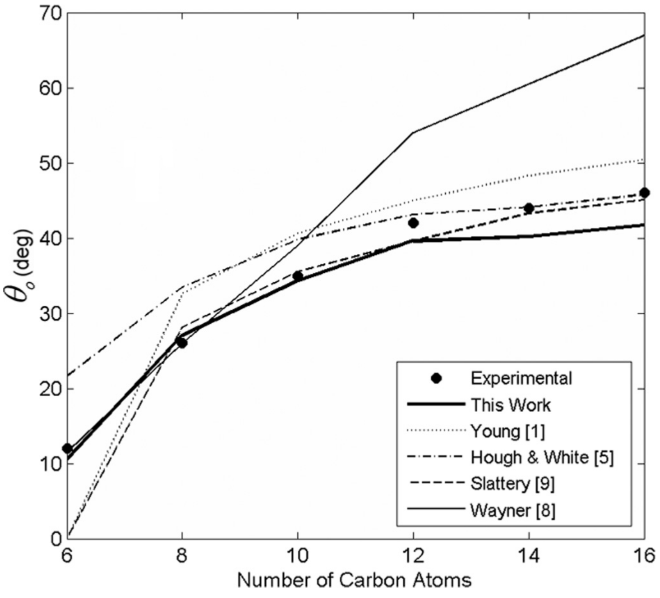

FIG. 2. Comparison of experimental contact angles of n-alkanes on PTFE with theoretical values predicted by several authors, including this work.

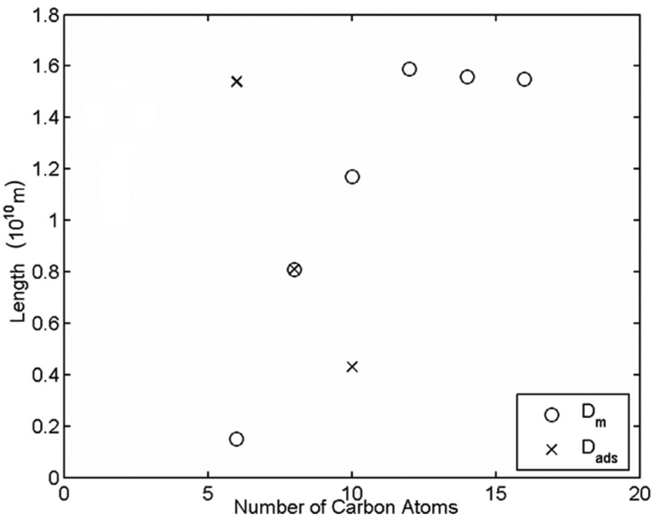

FIG. 3. Variation of the molecular cutoff length D_m and of adsorbed film thickness D_{ads} of n-alkanes on PTFE against the number of carbon atoms of the hydrocarbon chain.

However, D_m is not simply the number of hydrocarbons in the hydrocarbon chain but it also reflects the arrangement and inclination of the liquid molecules on the solid surface, and for a larger number of carbon atoms the molecular cutoff distance levels off. From Eq. (7) and using the values of σ and A_{LL} from Table II, we can verify that the relationship $\sqrt{A_{LL}/\sigma}$ remains essentially constant for a number of carbon atoms larger than 11. The adsorbed film is not necessarily a continuous film but clusters of liquid molecules attached to specific sites on the solid surface. Thus, adsorbed film thickness increases with decreasing number of carbon atoms. Unfortunately there is no reliable adsorption data for longer hydrocarbon chains but we could expect D_{ads} also to level off for longer chains due to the varying inclination of adsorbed molecules.

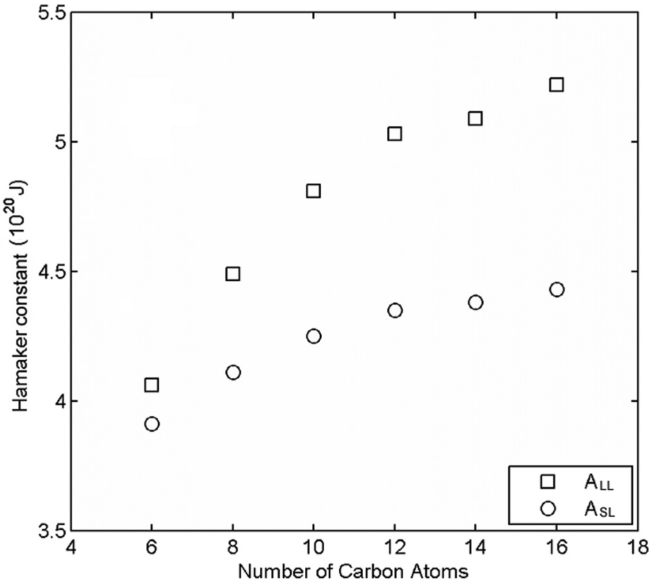

FIG. 4. Variation of Hamaker constants A_{LL} and A_{SL} of n-alkanes on PTFE with the number of carbon atoms of the hydrocarbon chain.

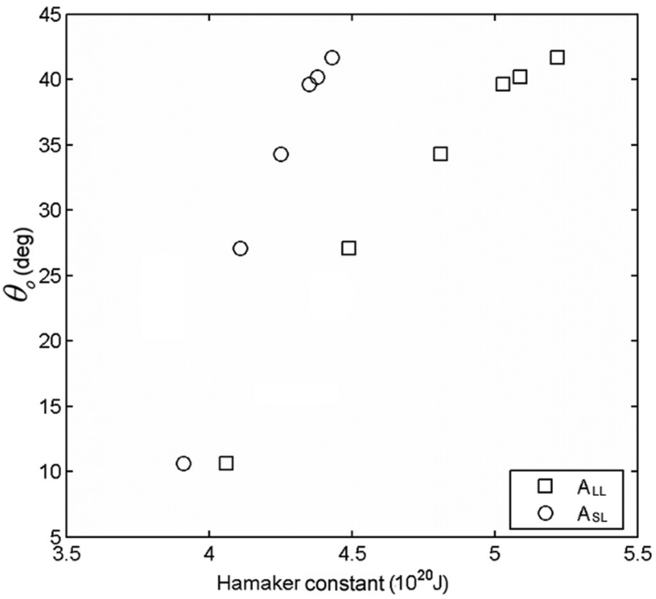

FIG. 5. Variation of the computed contact angle of n-alkanes on PTFE as a function of Hamaker constants A_{LL} and A_{SL}.

Figure 4 shows variation of Hamaker constants A_{LL} and A_{SL} with the length of the hydrocarbon chain. Regardless of the actual values of these constants it is noticeable that the difference between the solid-liquid attraction A_{SL} and the liquid-liquid attraction A_{LL} decreases as the number of carbon atoms decreases. Contact angles are determined by the balance of forces at the contact line: Attraction between solid and liquid molecules tends to increase spreading while attraction between liquid molecules tends to prevent spreading. As a consequence, decreasing the difference between these opposing forces results in smaller contact angles, as shown in Fig. 5. When the difference between attractive forces vanishes, as is the case with pentane, the contact angle becomes zero and the liquid film spreads uniformly over the solid surface without a visible bulk liquid phase.

For many years, and it is still true of current, physical chemistry textbooks, contact angles were defined using Young's relationship. However, the accurate contact angle predictions presented in Table II are not only evidence of the strong link between adsorption and contact angles but they also confirm the molecular dependency of contact angles.

IV. CONCLUSIONS

Adsorption upon a solid surface and equilibrium contact angles are two effects with the same cause—the balance of forces due to attraction of molecules in the vapor or liquid phase to sites on the solid surface and attraction of liquid molecules to other liquid molecules in the bulk phase. The presence of the adsorbed film near a three-phase contact line is a consequence of the volatility of the liquid phase. Molecules of liquid evaporate from the liquid phase and are adsorbed on the solid surface reaching a configuration where a submolecular film is in direct contact with and in mechanical equilibrium with an adjacent bulk liquid phase. The presence of an adsorbed film next to a static vapor-liquid-solid contact line modifies the balance of forces between the solid and the bulk liquid, and so affects the disjoining pressure and the value of the static contact angle—the effects of which are expressed quantitatively in Eq. (5).

It is important to point out that none of the previous equations for predicting contact angles, shown in Table I, introduce the effect of an adsorbed film. In fact many of them have constants that, by the way they are justified, may be considered as adjustable, *ad hoc* constants. The interesting thing about Eq. (5) is that it clearly introduces the presence of the adsorbed film and has no adjustable parameters. All four parameters included have a clear physical meaning and can be measured experimentally.

The ability of Eq. (5) to predict static contact angles is evaluated through the study of linear hydrocarbons on PTFE where theoretical contact angles are compared with experimental observations. The theoretical prediction of the contact angle is satisfactory and improves previous analyses, mainly for alkanes with a low number of carbon atoms for which adsorption is significant. The lack of experimental data precludes a more complete comparison with other nonpolar fluids and alternative substrates. Moreover, many other sets of data are incomplete—missing one or two of the four required parameters—and this should be an incentive to generate additional, experimental data.

The analysis presented here is limited to the simple equation of state of nonpolar fluids but it can be extended to more complex types of fluids and molecular forces. The steps to develop an expression for disjoining pressure for polar and more complex fluids are already known and alternative adsorption isotherm formulations are readily available. Finally, learning from the Landau-Levich [18] formulation for the drag-out of a solid from a viscous liquid, the thickness of entrained films and dynamic contact angles are closely related to the static contact angle in low Reynolds number flows. We can confidently expect therefore, that dynamic contact angles in wetting or dewetting problems at low Reynolds number will also be affected by molecular forces.

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