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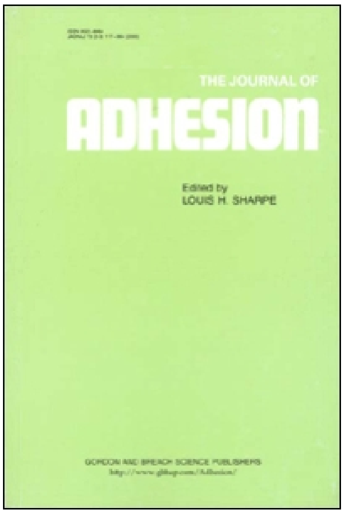

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Anisotropic Wetting of Liquids on Finely Grooved Surfaces†

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A photolithographically-prepared, parallel-grooved surface on silica has been employed as a model to study the influence of roughness on the spreading equilibrium of liquid drops. The equations generated by Oliver, Huh and Mason for cylindrically shaped drops were extended to account for wetting by liquid crystals. The observed drop shapes were dependent upon surface roughness. The equilibrium contact angles on a smooth surface can be calculated from the roughness, contact angles both parallel and perpendicular to the grooves, and the drop shape. Reasonably good agreement with experimental contact angles was obtained.

KEY WORDS Anisotropic wetting; contact angles; grooved surfaces; liquid crystals; periodic roughness; spreading equilibrium.

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INTRODUCTION

Surfaces with periodic roughnesses and specific surface interactions appear to be able to orient and align liquid crystal molecules. Recently, Berreman[1] and Wolff, *et al.*,[2] have suggested that alignment of liquid crystal molecules on surfaces of microscopic parallel grooves is associated with an elastic distortion energy, which is a function of the surface contour and the average elastic modulus of the liquid crystal. Surfaces formed either by oblique evaporation of SiO_2[3] or rubbing,[4] are uncontrolled and difficult to reproduce or quantify. By using gratings with grooves of known dimension, which are fabricated using conventional photo-

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lithographic techniques, Flanders, Shavers and Smith[5] have produced specific alignments of liquid crystals.

Although our primary reason for investigating grooved surfaces is their potential ability to orient liquid crystals, our initial effort is directed to understanding the wetting of these surfaces by liquid crystals. Perhaps the most careful and quantitative examination of the wetting by liquids on well-characterized roughened surfaces is due to Johnson and Dettre[6,7,8] and more recently to Oliver, Huh and Mason (O, H and M).[9] These authors (O, H and M) have utilized a mechanistic rather than a thermodynamic approach to discuss the wetting of parallel-grooved surfaces. Under certain conditions, liquid drops become distorted resulting in elongated shapes. For the almost spherical drop, on a parallel grooved surface, the equation of Cassie and Baxter[10] appears valid. However, O, H and M find for other types of roughened surfaces the general applicability of the Cassie–Baxter equation is not warranted. From a balance of interfacial forces, O, H and M derive an expression for cylindrically shaped drops which relates θ_a, the contact angle parallel to the groove direction, to the surface roughness. Although O, H and M cite that their elongated drops are cylindrical, we have observed, for liquid crystal drops, that even for ratios of length to width of at least 5, the drops still appeared to have spherical caps when viewed parallel or perpendicular to the grooved surface. Consequently, we have modified the expressions derived by O, H and M to include both radii of curvature.

Mathematical analysis

O, H and M[9] considered a balance of forces for spherical and cylindrical drops on parallel grooved surfaces across a plane bisecting the drops lengthwise (Figure 1). Acting across the whole cross sectional area A of the bisected drop, the capillary pressure ΔP is opposed by surface tension forces, γ, of the free liquid surface pulling over its circumference S normal to the cross-section. In addition, there will be a horizontal component of γ acting on the solid locally along the contact line, resulting in

$$\Delta PA - \gamma S - \gamma L_{LV} + \gamma L_{SL} \cos \theta_0 = 0 \qquad (1)$$

where θ_0 is the equilibrium contact angle for a smooth surface and

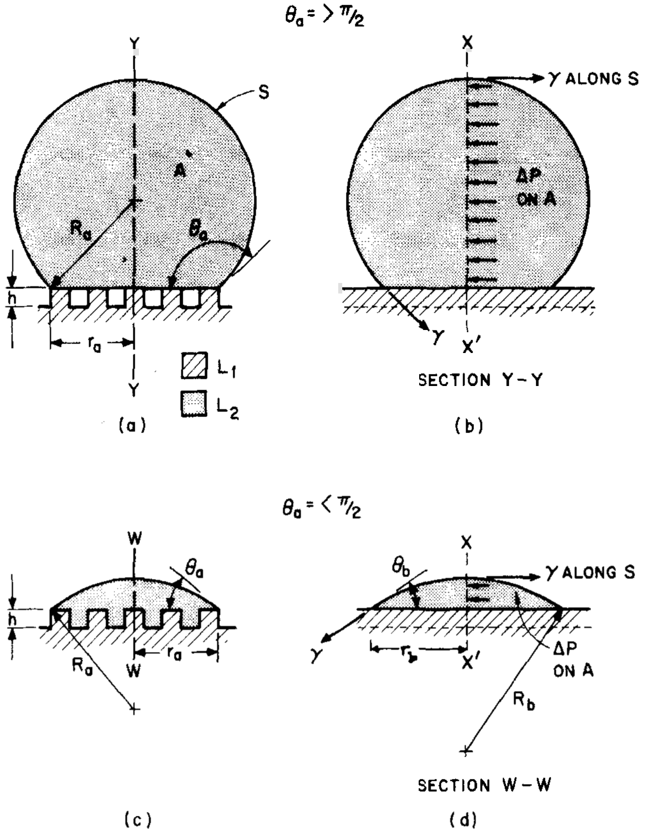

FIGURE 1 Equilibrium of liquid drops on parallel-grooved surfaces. (a) Cross-sectional view at the bisecting plane (shown by XX′ in (b)) of a spherical drop. For low-wetting liquids ($\theta_0 > 90°$), a composite surface is formed on the solid consisting of solid–liquid and liquid–void (dotted) interfaces. (b) Side view of the spherical drop. Broken lines indicate the contact line for the liquid-void interface and drop profile over the grooved area. (c) Cross-sectional view and (d) side view of a cylindrical drop. For high-wetting liquids ($\theta_0 < 90°$) a non-composite surface is formed.

L_{LS} and L_{LV} are the respective cross-sectional arc lengths of solid-liquid and liquid-void interfaces at the bisecting plane. A similar argument, using a free energy approach, likewise yields Eq. 1.[11] Since we observed the drops to be approximately spherical caps both parallel and perpendicular to the grooved surface, the capillary

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pressure to a first approximation may be written as

$$\Delta P = \gamma\left(\frac{1}{R_a} + \frac{1}{R_b}\right) \tag{2}$$

where R_a and R_b are the two radii of curvature, a denotes the direction parallel to the groove and b is perpendicular to the groove direction. A complete analysis of the surface contour of the drop is beyond the scope of the present study. From simple geometry, Figure 1, we obtain,

$$\begin{aligned} A &= R_a^2[\theta_a - \sin\theta_a \cos\theta_a] \\ S &= 2R_a\theta_a \\ r_a &= R_a \sin\theta_a \\ r_b &= R_b \sin\theta_b \end{aligned} \tag{3}$$

where θ_a and θ_b are the contact angles parallel and perpendicular to the groove direction, respectively. Inserting Eqs. 2 and 3 into Eq. 1 yields

$$\left[\frac{L_{SL}\cos\theta_0}{2r_a} - \frac{L_{LV}}{2r_a}\right] = \tfrac{1}{2}\left[\cos\theta_a + \frac{\theta_a}{\sin\theta_a}\right] + \tfrac{1}{2}\left(\frac{r_a}{r_b}\right)\left(\frac{\sin\theta_b}{\sin\theta_a}\right)\left[\cos\theta_a - \frac{\theta_a}{\sin\theta_a}\right] \tag{4}$$

which differs from the equation of O, H and M by the last term on the right hand side of Eq. 4. In the two limiting cases when $R_a = R_b$ and $R_b = \infty$, Eq. 4 yields the equations derived by O, H and M.[9]

Clearly, when $R_a = R_b$,

$$\frac{L_{SL}\cos\theta_0}{2r_a} - \frac{L_{LV}}{2r_a} = \cos\theta_a \tag{5}$$

Equation 5 is the Cassie and Baxter equation for composite surfaces. If there is no void space ($L_{LV} = 0$), $L_{SL}/2r_a$ becomes the conventional area ratio and Eq. 5 reduces to the Wenzel relation.[12] O, H and M state that the Cassie–Baxter equation is valid only for parallel grooves. The general application for Eq. 5 for other types of roughened surfaces is not warranted. If, as in the work of O, H

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and M, R_b is considered infinite, the drop being truly cylindrical,

$$\frac{L_{SL}\cos\theta_0}{2r_a}-\frac{L_{LV}}{2r_a}=\tfrac{1}{2}\left[\cos\theta_a+\frac{\theta_a}{\sin}\,\theta_a\right] \tag{6}$$

we obtain Eq. 3 of O, H and M.[9]

In the experiments described below, we test the applicability of Eq. 4 for the wetting of modified silica surfaces by liquid crystals, glycerol, and mercury. In addition, we re-examine the earlier data of Good, *et al.*,[13] and show how use of Eq. 4 may account for their observed anisotropic wetting behavior.

EXPERIMENTAL

(a) Surface preparation

Parallel-grooved surfaces were prepared on silica using conventional photolithographic techniques.[14] Four distinct regions of varying groove separations were prepared on one piece of silica. Figure 2 is a composite showing the uniformity of the four regions. The array is a square grating with periodicity (ridges and valleys) varying from 2 to 5 μm and depth of 1 μm. Clearly, the photolithographic techniques used for forming these surfaces yield an array of parallel grooves. Since the liquid crystals and glycerol will spread on silica along the groove direction, not yielding discrete elongated drops, the silica surfaces were rendered oleophobic by depositing ~40 Å of a fluoropolymer. The thickness of the fluoropolymer, which is formed by exposing C_2F_4 to a glow discharge,[15] was monitored by the change in frequency of a quartz crystal.

(b) Drop formation

To ascertain the effect of the grooved surface on the shape of the sessile drop, glycerol, mercury and two liquid crystals were employed. Small drops were placed onto these surfaces from a hypodermic needle. The glycerol has a surface tension of 63.4 mJ/m^2 and a viscosity of 9.45*p* at 23°C. P′-methoxybenzylidene-p-n-butylaniline (MBBA) has a surface tension of 30 mJ/m^2 and a viscosity of ~1.0*p* at 23.5°C. Licristal–Nematic

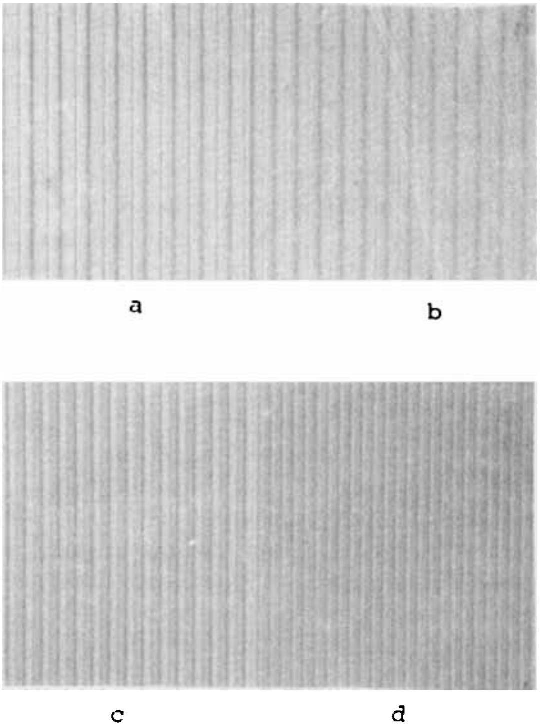

FIGURE 2 Parallel grooved square grating in silica. Four different surface roughnesses are represented. (a) $R = 1.20$, (b) $R = 1.25$, (c) $R = 1.33$, (d) $R = 1.50$. $R = 1 + h/L$.

Phase V is a mixture of liquid crystals having a surface tension of $30\,\text{mJ/m}^2$ and viscosity similar to MBBA. Mercury has a surface tension of $485\,\text{mJ/m}^2$ and a viscosity of ~$0.02p$ at 23°C. The surface tensions of the liquid crystals and glycerol were measured using a Du Nuoy tensionmeter. The surface tension of mercury was taken from the literature.

(c) Contact angle measurements and drop dimensions

Contact angles were measured parallel and perpendicular to the groove direction as well as on the smooth surface using a Rame–

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Hart contact angle goniometer. The dimensions of the drops were measured from photographs taken at 10× with a Polaroid camera. As in the study of O, H and M, drop sizes were sufficiently small such that gravitational effects were negligible and therefore excluded from consideration.

Contact angles were measured on both sides of the drop and the average values reported. The average deviation for the contact angle of liquids on the fluoropolymer modified silica is $\leq 2°$.

RESULTS AND DISCUSSION

When silica surfaces were used without the deposited fluoropolymer, we noted, as did O, H and M, that tongues of liquid extended ahead of the drop in the groove (Figure 3). However, with the fluoropolymer coating, we observed no extension of liquid beyond the drop perimeter.

Figures 4–7 illustrate the effect of uniform surface roughness on the wetting of two liquid crystals, glycerol and mercury. For $\theta_0 < 90°C$, the greater the surface roughness, $(1 + h/L)$, the more

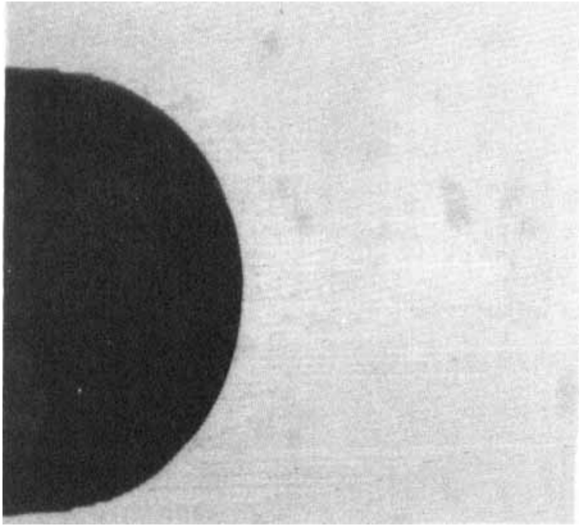

FIGURE 3 Tongues of liquid penetrating channels.

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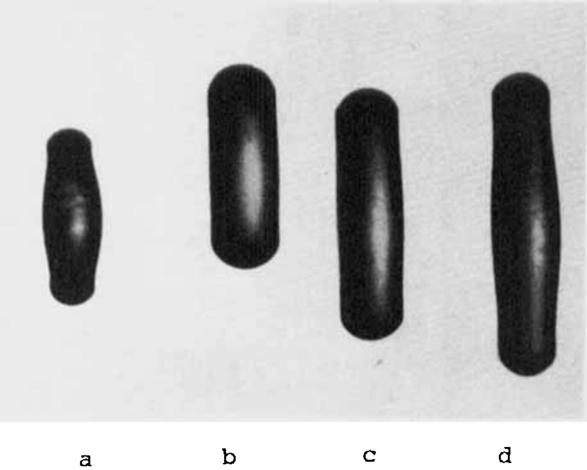

FIGURE 4 Wetting by MBBA on fluoropolymer coated silica. Surfaces are those represented in Figure 2.

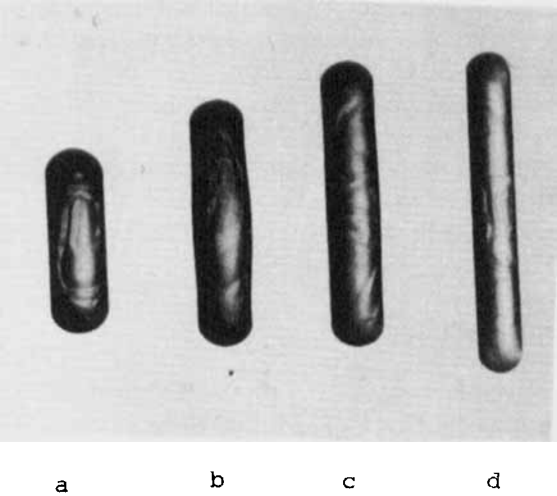

FIGURE 5 Wetting by Licristal–Nematic Phase V on fluoropolymer coated silica. Surfaces are those represented in Figure 2.

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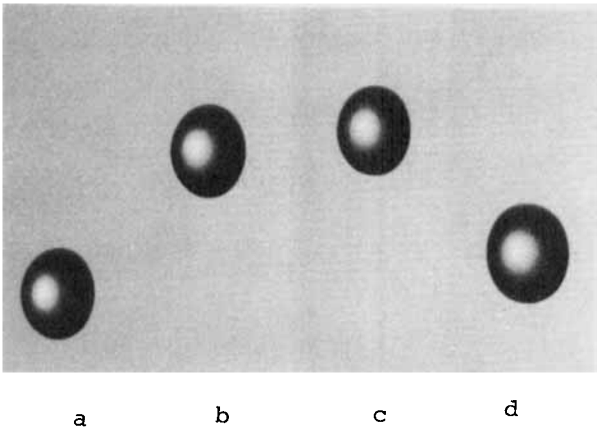

FIGURE 6 Wetting of Glycerol on Fluoropolymer coated silica. Surfaces are those represented in Figure 2.

pronounced the extent of drop elongation (see derivation in the appendix). Initially, we employed the analysis of O, H and M, but the computed θ_0 values were inconsistent. We were able to account for the discrepancy by including in the analysis the contact angle both parallel and perpendicular to the groove direction as well as the ratio of the drop diameters (Eq. 4). The data in Table I in

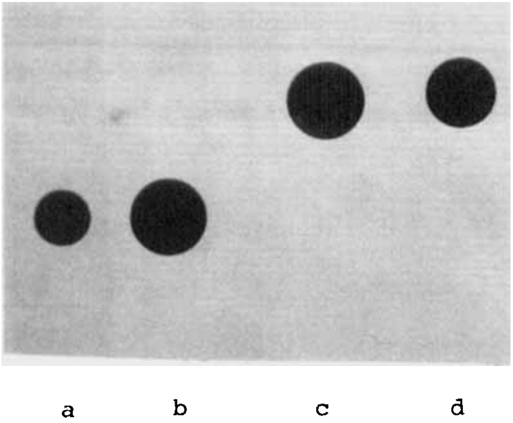

FIGURE 7 Wetting by mercury on fluoropolymer coated silica. Surfaces are those shown in Figure 2.

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TABLE I

Wetting of anisotropic drops of liquids on a fluoropolymer coated square grating on silica

Liquid	L_1	L_2	h	R	$2r_a$	$2r_b$	θ_a	θ_b	$\theta_{o\text{calc}}$
	μm	μm	μm		mm	mm			
MBBA	5	5	1	1.20	0.95	3.05	110	47	62
	4	4	1	1.25	1.00	4.05	109	49	61
	3	3	1	1.33	0.90	4.70	120	43	63
	2	2	1	1.50	0.73	5.25	120	35	63
								$(\theta_0)_{\text{exp}}$	61
Licristal-Nematic Phase V	5	5	1	1.20	0.98	2.85	122	58	67
	4	4	1	1.25	1.15	3.35	120	55	67
	3	3	1	1.33	1.10	4.10	118	52	63
	2	2	1	1.50	1.10	4.95	117	48	64
								$(\theta_0)_{\text{exp}}$	62
Glycerol	5	5	1	1.20	1.23	1.48	125	105	95
	4	4	1	1.25	1.23	1.50	125	111	88
	3	3	1	1.33	1.20	1.45	125	112	87
	2	2	1	1.50	1.35	1.63	126	111	92
								$(\theta_o)_{\text{exp}}$	95

conjunction with Eq. 4 are used to compute the equilibrium contact angles for a smooth surface, θ_0. The agreement is quite satisfactory when compared to the measured θ_0.

When the data of Table I were included in Figure 8, (Figure 5 of Reference 9), we observed discrepancies for $\theta_a \sim 90°$.

From Eq. 4, if $\theta_a = 90°$,

$$\frac{L_{SL}}{2r_a}\cos\theta_0 - \frac{L_{LV}}{2r_a} = \frac{\pi}{4}\left[1 - \frac{r_a}{r_b}\sin\theta_b\right] \tag{7}$$

For a parallel grooved surface, when $\theta_a \sim 90°$, we find that $\theta_b < \theta_a$ and $r_a < r_b$. Under these circumstances, Eq. (7) predicts

$$\frac{L_{SL}}{2r_a}\cos\theta_0 - \frac{L_{LV}}{2r_a} < \pi/4 \tag{8}$$

which is confirmed by plotting the data of Table I in Figure 8.

Equation (A.5) suggests that for spherical drops on parallel-grooved surfaces, where the number of grooves, $N \gg 1$, $L_{SL} = L_{LV}$ and $\theta_0 > 90$, the contact angle of a liquid on the roughened surface

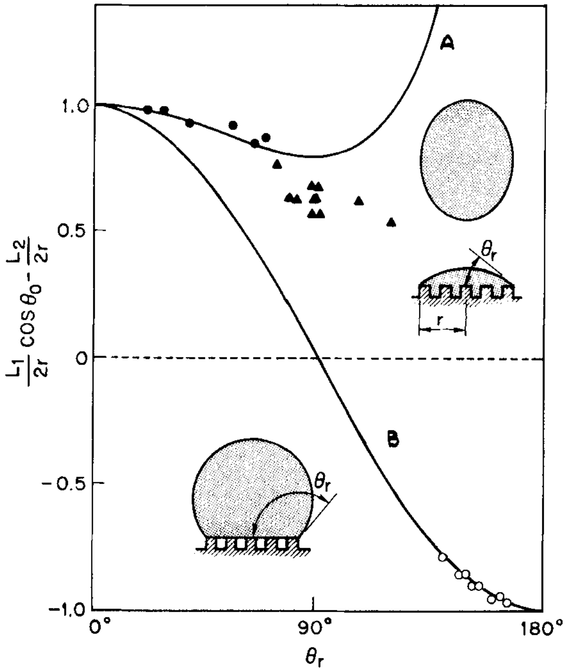

FIGURE 8 Measured values of the apparent advancing contact angle θ_a for approximately spherical drops of mercury (open points) and for nearly-cylindrical drops of PPE (closed points). The solid lines are calculated from Eq. (2) (curve A), and Eq. (3) (curve B), both of Ref. 9. Note for curve A, when $\theta_r < 90°$, $L_{LV}/2r$ becomes zero and Eq. (2)[9] reduces to Wenzel's equation. The triagnles are from this study.

is independent of the roughness. To test this hypothesis, drops of mercury were placed on the roughened surfaces and the values of θ_a measured. The results in Table II lend credence to the analysis. Indeed, the values of θ_a are essentially independent of the surface roughness. When θ_0 is close to 90°, as in the case of glycerol, there is some deviation from being spherical the drop is slightly elliptical.

Since we observed that the drop is a spherical segment both parallel and perpendicular to the groove direction, it is clear from Figure 1 that

$$\frac{h_a}{r_a} = \frac{1 - \cos\theta_a}{\sin\theta_a}$$

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TABLE II
The wetting of mercury on the square array fluoropolymer modified silica surface

Roughness $(1+h/L)$	r_a/r_b	θ_a	θ_0
1.00	1.0	130	130
1.20	1.0	141	124
1.25	1.0	142	125
1.33	1.0	145	130
1.50	1.0	148	137

and

$$\frac{h_b}{r_b}=\frac{1-\cos\theta_b}{\sin\theta_b}$$

where h is the depth of the groove. Since $h_a=h_b$,

$$r_a\left[\frac{1-\cos\theta_a}{\sin\theta_a}\right]=r_b\left[\frac{1-\cos\theta_b}{\sin\theta_b}\right] \tag{9}$$

The data in Table III indicate the Eq. (9) holds reasonably well

TABLE III
Test for spherical segment of drop parallel and perpendicular to groove direction

R	r_o	θ_a	$r_o\left\{\frac{1-\cos\theta_a}{\sin\theta_a}\right\}$	r_b	θ_b	$r_b\left\{\frac{1-\cos\theta_b}{\sin\theta_b}\right\}$
MBBA						
	mm			mm		
1.20	0.48	110	0.69	1.53	47	0.67
1.25	0.50	109	0.70	2.03	49	0.93
1.33	0.45	120	0.86	2.35	43	0.93
1.50	0.37	120	0.71	2.63	35	0.83
Licristal Nematic Phase V						
1.20	0.49	122	0.88	1.43	58	0.79
1.25	0.58	120	1.00	1.68	55	0.87
1.33	0.55	118	0.92	2.05	52	1.00
1.50	0.55	117	0.90	2.48	48	1.10
Glycerol						
1.20	0.62	125	1.19	0.74	105	0.96
1.25	0.62	125	1.19	0.75	111	1.09
1.33	0.61	125	1.17	0.73	112	1.08
1.50	0.68	126	1.33	0.92	111	1.19

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TABLE IV
Contact of *n*-hydrocarbons on stained (160%) teflon FEP*

Liquid	θ_a	θ_b	r_a/r_b	$(\theta_o)_{\text{meas}}$	$(\theta_o)_{\text{calc}}$ Eq. 4
n-hexadecane	60.0	49.0	0.78	55.0	54.0
n-tetradecane	57.6	45.9	0.78	51.8	52.0
n-dodecene	53.5	42.5	0.78	47.8	48.7
n-decane	48.9	39.1	0.78	43.6	45.8
n-octane	41.1	31.1	0.78	36.0	38.6
ethylene glycol	100.0	91.7	0.85	92.3	92.4

confirming the need to consider both radii of curvature in a complete analysis.

In an earlier study of the spreading of liquids on roughened polymer surfaces, Good, Kvikstad and Bailey[13] rejected the concept of surface roughness as being responsible for elongated shapes of drops in favor of an anisotropic force field. Unfortunately, they presented no quantitative analysis since there is no orderly roughness as in the case studied by Flanders, *et al.*[5]

Unfortunately, Good, Kvitstad and Bailey report only the θ_a and θ_b values for n-hydrocarbons on the highly strained fluoropolymer. However, if we assume that Figure 1 of their paper represents the drop dimensions for all the hydrocarbons and that the surface has a roughness of 1.05, which is entirely reasonable from their photomicrographs, we can compute θ_0 from Eq. (4). The results of these calculations are in Table IV. Clearly, the agreement is quite satisfactory. We include also the case of the more polar liquid ethylene glycol. Here, to get reasonable agreement the ratio r_a/r_b is taken to be about 0.85.

Although Good, Kvikstad and Bailey conclude that an anisotropic force field is responsible for the elongated drops, the introduction of a modest surface roughening can account for this deviation from circularity. We feel that the results of their study are better interpreted using roughness as the criterion for elongated drops rather than invoke a difficult-to-analyze anisotropic force field.

Acknowledgement

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study. I should also like to thank M. Sammon and S. Meiboom for their fluoropolymer deposition and their valuable discussions.

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Appendix

SURFACE ROUGHNESS OF SQUARE ARRAY $\theta_0 < 90°$

If n = number of grooves, then the solid-liquid contact area for a drop of $\theta_0 < 90°$, covering n grooves (Figure 1A) in a square well

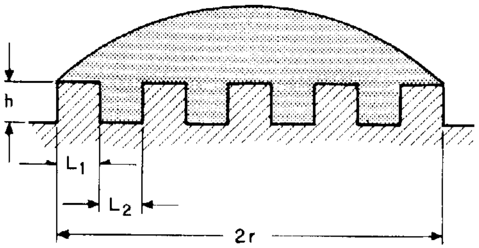

FIGURE 1A Schematic of sessile drop on a surface of n parallel grooves.

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array is

$$(n+1)L_1 + nL_2 + 2nh = L_{SL}$$

where

$$2r = (n+1)L_1 + nL_2$$

In the above situation there is only solid–liquid interfacial contact and

$$\frac{L_{SL}}{2r_a}\cos\theta_0 = \left[1 + \frac{2nh}{[(n+1)L_1 + nL_2]}\right]\cos\theta_0 \tag{A1}$$

If $n \gg 1$ and $L_1 = L_2$,

$$\left(1 + \frac{h}{L}\right)\cos\theta_0 = \left(\frac{L_{SL}}{2r_a}\right)\cos\theta_0 \tag{A2}$$

where $(1 + h/L)$ is a measure of the surface roughness.

Surface roughness of square array $\theta_0 > 90^0$

For a composite interface where we have both solid–liquid and liquid–vapor interfaces,

$$\frac{L_{SL}}{2r_a}\cos\theta_0 - \frac{L_{LV}}{2r_a} = \frac{(n+1)L_1\cos\theta_0 - nL_2}{(n+1)L_1 + nL_2} = \cos\theta_a \tag{A3}$$

If $n \gg 1$ and $l_1 = L_2$,

$$\frac{L_{SL}}{2r_a}\cos\theta_0 - \frac{L_{LV}}{2r_a} = \frac{\cos\theta_0 - 1}{2} = \cos\theta_a \tag{A4}$$

or

$$\cos\theta_0 = 2\cos\theta_a + 1 \tag{A5}$$

Consequently, for a spherical drop $(\theta_0 > 90^0)$ on a parallel square array where $L_1 = L_2$ and $n \gg 1$ the contact angle should be reasonably independent of surface roughness.