How Wenzel and Cassie Were Wrong

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We argue using experimental data that contact lines and not contact areas are important in determining wettability. Three types of two-component surfaces were prepared that contain "spots" in a surrounding field: a hydrophilic spot in a hydrophobic field, a rough spot in a smooth field, and a smooth spot in a rough field. Water contact angles were measured within the spots and with the spot confined to within the contact line of the sessile drop. Spot diameter and contact line diameter were varied. All of the data indicate that contact angle behavior (advancing, receding, and hysteresis) is determined by interactions of the liquid and the solid at the three-phase contact line alone and that the interfacial area within the contact perimeter is irrelevant. The point is made that Wenzel's and Cassie's equations are valid only to the extent that the structure of the contact area reflects the ground state energies of contact lines and the transition states between them.

Introduction

The first issue that we address and justify in this paper is the pejorative and provocative tone of the title; we believe that it is appropriate and necessary. We review the substance of Wenzel's and Cassie's theories immediately following these opening remarks but first explain our choice of title. Figure 1 plots the citations versus calendar year for the past decade to three papers that were published over 60 years ago. An exponentially increasing number of publications citing Wenzel[1] and Cassie[2] have appeared in recent years. This increase is due almost entirely to reports of "superhydrophobic" surfaces. The authors of these papers make use of the Wenzel and Cassie theories casually and do not cite work (discussed below) that questions these perspectives. In particular, Pease[3] first discussed the fact that wettability as measured by contact angle is a one-dimensional issue. His publication (Figure 1) has essentially been ignored, while the Wenzel and Cassie equations have become part of surface science education and are concepts that most of today's surface scientists believe and take for granted. We attempt here to correct this misconception.

When a drop of liquid contacts a surface, one of two phenomena generally[4] occurs (1) the liquid wets the surface; a circular three-phase contact line is formed that continues to increase in radius and liquid spreads over the entire surface, (2) the droplet contacts the surface and the three-phase contact line advances to a certain radius and stops, creating a sessile droplet in the shape of a section of a sphere with a contact angle that depends on the chemical compositions of the liquid and the surface and the topography of the surface. Which of these phenomena occurs and the value of the contact angle that forms in the second case are described in quantitative terms by Young's equation (eq 1), which relates the contact angle to the three interfacial free energies

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

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(1) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.
(2) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546.
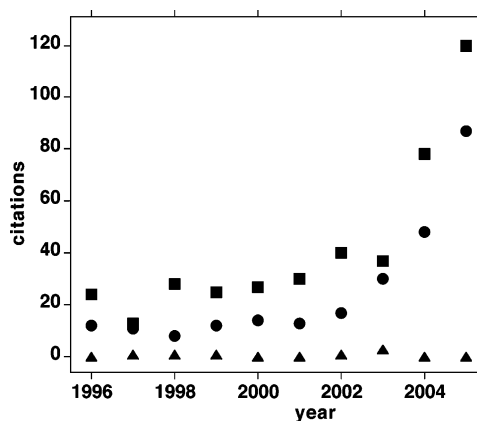(3) Pease, D. C. *J. Phys. Chem.* **1945**, *49*, 107.

Figure 1. Citations versus publication year: (■) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988, (●) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546, (▲) Pease, D. C. *J. Phys. Chem.* **1945**, *49*, 107.

involved: solid−vapor, liquid−vapor, and solid−liquid. This equation is instructive and explains commonly observed phenomena that are counterintuitive to some, for instance why water (high γ_{LV}) beads up on hydrocarbon surfaces (low γ_{SV}) but hydrocarbon liquids (low γ_{LV}) spread on ice (high γ_{SV}) (or on water). Liquids spread on surfaces when $\gamma_{SV} - \gamma_{SL} \geq \gamma_{LV}$ (cos $\theta \geq 1$, $\theta = 0$), form contact angles of 90° when $\gamma_{SV} = \gamma_{SL}$ (cos $\theta = 0$) and form contact angles higher than 90° when $\gamma_{SV} < \gamma_{SL}$ (cos θ is negative).

The units of the γ's in eq 1 are erg/cm^2 (energy per unit area), and we have been taught and have learned to think in these terms (energy per unit area). The units can also be expressed as dyn/cm, and the discussion below suggests that these units (force/length) give a more intuitive meaning. Wenzel[1] realized that when a droplet contacts a rough surface and forms a sessile droplet with a smooth liquid−vapor interface, but rough (more surface area) liquid−solid and solid−vapor interfaces, Young's equation (eq 1) should be modified by multiplying the numerator of the right side of eq 1 by a roughness factor, r, that is the actual

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(4) Gao, L.; McCarthy, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9052. A third phenomenon, complete rejection of the droplet by a surface with contact angles of 180°, is possible, and we have recently reported a surface with this behavior.

contact area divided by the projected area of surface that the droplet contacts (eq 2). This makes intuitive

$$\cos \theta_{\text{rough}} = r \cos \theta_{\text{smooth}} \tag{2}$$

sense to most people trained in thermodynamics and reinforces the concept that the area of contact between the liquid and solid should affect the contact angle. Cassie[2] addressed the issue of composite surfaces and proposed eq 3 to predict the

$$\cos {}^c\theta = f_1 \cos \theta_1 + f_2 \cos \theta_2$$
$$f_1 + f_2 = 1 \tag{3}$$

contact angle (${}^c\theta$) of a binary composite surface containing two components with contact angles of θ_1 and θ_2 and area fractions of f_1 and f_2. Again the concept of contact area was reinforced. One might conclude (many authors have) that equilibrium interfacial free energies (the right side of eq 1) dictate wettability and that Wenzel's and Cassie's equations (the right side of eq 1 can be substituted for $\cos \theta$ in these equations) can be applied to predict or explain real (rough and composite) surface behavior. This has been used in research many times; the observation that there is a transition between the Wenzel and Cassie regimes was first addressed by Johnson and Dettre,[5] and this behavior has been discussed in significant detail.[6-15]

The theories behind eqs 2 and 3 are somewhat consistent with the observed data for many surfaces that have been studied over the past 50 or so years, but many examples of where they are inconsistent have also been reported.[16] More complex and more sophisticated models for rough and composite surfaces have also been proposed.[16,17]

We contend here that the predictions of these theories and the extent to which data are consistent with them are somewhat fortuitous, but not right. This is not a new contention and is essentially the same point that has been made weakly several times in the past. Pease[3] did not, in 1945, directly question these theories but clearly suggested the ideas behind the questioning. Bartell directly questioned[18] Wenzel's theory in 1953 and showed that the contact angles of droplets on surfaces containing roughness within the contact line were identical to those of smooth surfaces. Extrand[16] showed that the three-phase structure at the contact line, not the liquid–solid interface beneath the droplet controls contact angle. He prepared surfaces with chemically heterogeneous islands that exhibited contact angles identical to surfaces without islands when the islands were in the interior of the contact line. We have stressed[19-24] that contact angle and hysteresis are a function of contact line structure and that the

(5) Johnson, R. E., Jr.; Dettre, R. H. *Adv. Chem. Ser.* **1964**, *43*, 112.
(6) Quere, D. *Physica A* **2002**, *313*, 32.
(7) He, B.; Patankar, N. A.; Lee, J. *Langmuir* **2003**, *19*, 4999.
(8) Bico, J.; Marzolin, C.; Quere, D. *Europhys. Lett.* **1999**, *47*, 220.
(9) Quere, D.; Lafuma, A.; Bico, J. *Nanotechnology* **2003**, *14*, 1109.
(10) Patankar, N. A. *Langmuir* **2003**, *19*, 1249.
(11) He, B.; Lee, J.; Patankar, N. A. *Colloids Surf., A* **2004**, *248*, 101.
(12) Lafuma, A.; Quere, D. *Nat. Mater.* **2003**, *2*, 457.
(13) Patankar, N. A. *Langmuir* **2004**, *20*, 8209.
(14) Patankar, N. A. *Langmuir* **2004**, *20*, 7097.
(15) Wier, K. A.; McCarthy, T. J. *Langmuir* **2006**, *22*, 2433.
(16) See: Extrand, C. W. *Langmuir* **2003**, *19*, 3793 and references cited therein.
(17) See: Lipowski, R.; Lenz, P.; Swain, P. S. *Colloids Surf.* **2000**, *161*, 3 and references cited therein.
(18) Bartell, F. E.; Shepard, J. W. *J. Phys. Chem.* **1953**, *57*, 455.
(19) Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Öner, D.; Youngblood, J.; McCarthy, T. J. *Langmuir* **1999**, *15*, 3395.
(20) Öner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777.
(21) Youngblood, J. P.; McCarthy, T. J. *Macromolecules* **1999**, *32*, 6800.
(22) Gao, L.; McCarthy, T. J. *Langmuir* **2006**, *22*, 2966.
(23) Gao, L.; McCarthy, T. J. *Langmuir* **2006**, *22*, 5998.
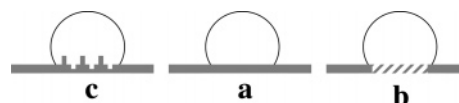(24) Gao, L.; McCarthy, T. J. *Langmuir* **2006**, *22*, 6234.

Figure 2. The Wenzel and Cassie equations predict that contact angles will differ from that of **a** when the surface beneath the droplet, away from the contact line, has a different chemistry (**b**) or topography (**c**).

kinetics of droplet movement, rather than thermodynamics, dictate wettability. With the exception of Bartell's paper,[17] the other publications[16,19-25] "tip-toed around" criticism of Wenzel and Cassie. Here we directly question them and show with detailed experiments, similar to those of Bartell and Extrand, that the theories are wrong.

Experimental Section

Contact angle measurements were made with a Ramé–Hart telescopic goniometer equipped with a Gilmont syringe and 24-gauge flat-tipped needle. The probe fluid was house-purified water (reverse osmosis) that was further purified using a Millipore Milli-Q system that involves reverse osmosis, ion-exchange, and filtration steps (10^{18} Ω/cm). Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively. The values reported are averages of 5–10 measurements made on different areas of the sample surface. Video recording was carried out on a home-built stage in the laboratory of Prof. A. J. Crosby. Silicon wafers were obtained from International Wafer Service (100 orientation, P/B doped, resistivity from 20 to 40 Ω·cm). They varied in thickness from 450 to 575 μm. (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane (PFA-(Me)$_2$SiCl) was purchased from Gelest and used without further purification.

Masks for surfaces **b** and **c** were prepared using AutoCAD and were printed on high-resolution transparencies. The procedure[26] is described and discussed in detail in ref 26.

All samples (untreated silicon wafers for surfaces **a** and photolithographed samples for surfaces **b** and **c**) were cleaned with oxygen plasma using a Harrick Plasma Cleaner immediately before surface modification. Samples were placed in a custom-designed (slotted hollow glass cylinder) holder and were suspended in a flask contain 0.5 mL PFA(Me)$_2$SiCl (the wafers did not make contact with the liquid). Vapor-phase reactions were carried out for 3 days at ∼70 °C.

Spots on surfaces **a** were prepared on a contact angle goniometer stage. Concentrated sodium hydroxide droplets were advanced on PFA(Me)$_2$SiCl-modified wafers to the desired spot diameter and allowed to remain in this position for 5 min. The samples were then rinsed with copious amounts of water.

Results and Discussion

The results that we present here are analogous to those of Bartell[17] and Extrand[16] and serve to emphasize the points that they and we have made in the past. No new concepts are introduced here, but an obvious minority view of wettability is consolidated and focused. Here we show with simple experiments that the Wenzel and Cassie equations are not directly relevant to water repellency and that events at the contact line, not over the liquid–solid interfacial area, control contact angle. Equations 2 and 3 predict that the contact angle will be affected by differences in surface chemistry or topography away from the contact line (Figure 2).

Three types of two-component surfaces were prepared and studied, one based on different chemistries and two based on different topographies. Schematic representations of them are

(25) Fadeev, A. Y.; McCarthy, T. J. *Langmuir* **1999**, *15*, 3759.
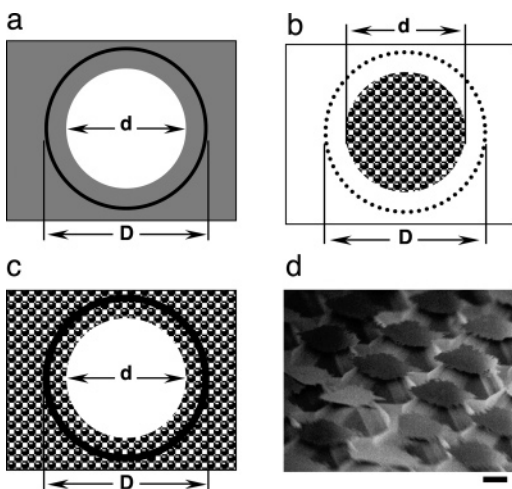(26) Ou, J.; Perot, B.; Rothstein, J. P. *Phys. Fluids* **2004**, *16*, 4635.

Figure 3. Depictions of (**a**) a hydrophilic spot in a hydrophobic field, (**b**) a rough spot in a smooth field, and (**c**) a smooth spot in a rough field. (**d**) SEM indicating the topography of the rough regions in **b** and **c**. *d* in **a**, **b**, and **c** indicates the spot diameter; *D* indicates the droplet diameter. The scale bar in **d** is 10 μm.

shown in Figure 3. Figure 3a depicts a surface with a hydrophilic spot in a hydrophobic field. These surfaces were prepared by partial hydrolysis of the smooth silicon-supported perfluoroalkyl surface, **PFA**. Figure 3b and c depicts surfaces of homogeneous
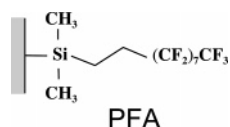
PFA composition, but with a rough spot in a smooth field (Figure 3b) and a smooth spot in a rough field (Figure 3c). These were prepared by photolithography prior to silanization. These surfaces are referred to as surfaces **a**, **b**, and **c** to correspond with Figure 3. Surfaces with three spot sizes, 1, 1.5, and 2 mm in diameter, were prepared for each type of surface. Figure 3d shows the topography of the spot and field in panels b and c of Figure 3, respectively.

Polished silicon wafers were treated in the vapor phase with $PFA(Me)_2SiCl$. This monofunctional reagent can react only[27] to form a covalently attached monolayer; no oligolayers form. When the silicon samples are rigorously clean, the monolayers produced exhibit reproducible contact angles of $\theta_A/\theta_R = 119°/110°$ and a 10 Å ellipsometrically determined thickness. This is not a close-packed monolayer, but is complete, albeit disordered.[24] If the wafers are not clean, or if the reaction is not allowed to go to completion, the receding contact angle is considerably lower.

Drops of saturated sodium hydroxide supported on a syringe tip were brought into contact with these surfaces on a contact angle goniometer stage and advanced to form sessile droplets of different diameter. This solution hydrolyzes the monolayer, exposing silanols on the surface, to form a hydrophilic "spot." Samples with hydrophilic spot diameters of 1, 1.5, and 2 mm (*d* in Figure 3 and Table 1) were prepared.

Table 1 shows water contact angle data recorded using sessile drops of varying contact diameter (*D* in Figure 3 and Table 1). Also shown are the area fractions of liquid−solid contact (f_1 and f_2 are the area fractions inside and outside the spot, respectively) and the contact angles calculated using eq 3, $\theta_A/\theta_R = 35°/10°$ for the area inside the spot and $\theta_A/\theta_R = 119°/110°$ for the outside region. Contact angles measured inside the spots were consistently

(27) Fadeev, A. Y.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7268.

Table 1. Contact Angles for Surfaces with a Hydrophilic Spot in a Hydrophobic Field (Surfaces a)

d (mm)	*D* (mm)	f_1	f_2	θ_A/θ_R (calcd)	θ_A/θ_R (obs)
1	0.5	1.00	0.00		33°/11°
1	1.5	0.44	0.56	85°/76°	119°/110°
1	2.0	0.25	0.75	99°/91°	118°/108°
1	2.5	0.16	0.84	106°/97°	119°/108°
1.5	0.7	1.00	0.00		35°/9°
1.5	2.0	0.56	0.44	76°/66°	120°/110°
1.5	2.5	0.36	0.64	91°/82°	118°/109°
1.5	3.0	0.25	0.75	99°/91°	120°/111°
2	0.7	1.00	0.00		35°/10°
2	2.5	0.64	0.36	70°/60°	120°/110°
2	3.0	0.44	0.56	85°/76°	119°/110°
2	3.5	0.33	0.67	93°/85°	118°/111°

Table 2. Contact Angles for Surfaces with a Rough Spot on a Smooth Field (Surfaces b)

d (mm)	*D* (mm)	f_1	f_2	θ_A/θ_R (calcd)	θ_A/θ_R (obs)
1	0.5	1.00	0.00		168°/132°
1	1.1	0.83	0.17	152°/122°	117°/81°
1	1.2	0.69	0.31	145°/115°	117°/82°
1	1.3	0.59	0.41	140°/108°	117°/81°
1.5	0.7	1.00	0.00		166°/134°
1.5	1.6	0.88	0.12	156°/125°	117°/82°
1.5	1.7	0.78	0.22	150°/119°	117°/81°
1.5	1.8	0.69	0.31	145°/115°	117°/82°
2	0.7	1.00	0.00		165°/133°
2	2.1	0.91	0.09	158°/126°	117°/82°
2	2.2	0.83	0.17	153°/122°	117°/81°
2	2.3	0.76	0.24	148°/118°	118°/82°

$\theta_A/\theta_R = \sim35°/\sim10°$ and in each instance, independent of *d*, *D*, f_1, or f_2, when the spot was within, but away from the contact line, $\theta_A/\theta_R = \sim119°/\sim110°$ was observed. The values predicted by eq 3 are meaningless. Only the small fraction of the surface probed by the contact line is important in affecting the contact angle behavior.

Two different types of surfaces with patterned topographical differences were prepared by photolithography. These are described in Figure 3b−d. Surfaces with 1, 1.5, and 2 mm diameter spots were prepared with differential topography. In surfaces **b**, the spots were rough and the field was smooth, and in surfaces **c**, the spots were smooth and the field was rough. After photolithography and cleaning, the samples were treated with $PFA(Me)_2SiCl$ in the vapor phase under identical conditions as those used to prepare surfaces **a**. We make four points concerning these samples: (1) They do not contain the clean photolithographed square posts that would be suggested from the photolithography masks. The wet chemical development etched the latent posts corrosively. (2) The surfaces contain many defects that pin drops and exhibit a "mixed Wenzel/Cassie" behavior. Below we analyze the data assuming a complete "Cassie state;" we emphasize that we could also have assumed a "Wenzel state" and calculated an effective roughness from the contact angle data. (3) The PFA monolayers that form on smooth sections of these samples contain defects that cause receding contact line pinning, and the contact angles observed are $\theta_A/\theta_R = \sim117°/\sim82°$ rather than $\theta_A/\theta_R = \sim119°/\sim110°$, which is observed on clean surfaces. (4) The samples are, however, perfectly adequate for the experiments described here, and we can prepare them in-house.

Tables 2 and 3 show data analogous to Table 1 for surfaces **b** and surfaces **c**, respectively. The contact angles used for calculating the values using eq 3 are $\theta_A/\theta_R = 117°/82°$ for the smooth areas (outside the spot for surfaces **b** and inside the spot for surfaces **c**) and $\theta_A/\theta_R = 168°/132°$ for the rough areas (inside
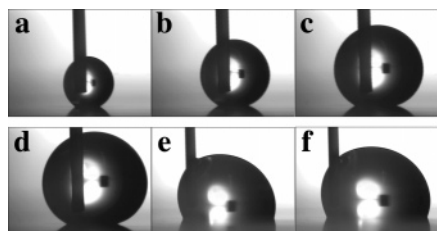
Figure 4. Selected frames of a videotape of a droplet advancing from a rough spot onto a smooth field.

Table 3. Contact Angles for Surfaces with a Smooth Spot on a Rough Field (Surfaces c)

d (mm)	D (mm)	f_1	f_2	θ_A/θ_R (calcd)	θ_A/θ_R (obs)
1	0.5	1.00	0.00		117°/82°
1	1.1	0.83	0.17	123°/90°	168°/132°
1	1.2	0.69	0.31	128°/96°	167°/132°
1	1.3	0.59	0.41	132°/101°	167°/132°
1.5	0.7	1.00	0.00		117°/82°
1.5	1.6	0.88	0.12	121°/88°	167°/132°
1.5	1.7	0.78	0.22	125°/92°	168°/132°
1.5	1.8	0.69	0.31	128°/96°	168°/131°
2	0.7	1.00	0.00		116°/82°
2	2.1	0.91	0.09	120°/86°	168°/132°
2	2.2	0.83	0.17	123°/90°	167°/132°
2	2.3	0.76	0.24	126°/93°	167°/131°

the spot for surfaces **b** and outside the spot for surfaces **c**). Both sets of data mirror what was observed for surface **a**: apparently smooth surfaces ($\theta_A/\theta_R = 117°/82°$) were observed for all values of d, D, f_1, or f_2 when a rough spot was within the contact line and apparently rough surfaces ($\theta_A/\theta_R = 168°/132°$) were observed in all cases when a smooth spot was within the contact line. Again and again the values calculated using eq 3 are meaningless.

Figures 4 and 5 show selected frames from videotapes of water drops being advanced on a surface **b** and a surface **c**, respectively. In Figure 4a–d, the droplet advances outward on a rough spot with a high advancing contact angle, similar to that measured with a goniometer ($\theta_A \approx 168°$). When it reaches the perimeter of the spot, it spreads onto the smooth surface (gravity is a driving force) and exhibits a lower contact angle (Figure 4e), similar to that measured with a goniometer ($\theta_A \approx 117°$). Note that the video camera had to zoom out (the needle is apparently thinner) to view the drop. This angle is maintained as the drop is further advanced (Figure 4f). In Figure 5a and b, a droplet in the center of a smooth spot exhibits a relatively low ($\theta_A \approx 117°$) contact angle and advances to the perimeter of the spot where it is pinned on the rough perimeter. The contact angle increases
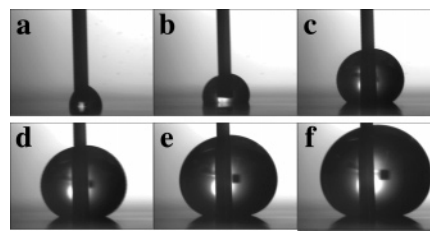

Figure 5. Selected frames of a videotape of a droplet advancing from a smooth spot onto a rough field.

with a pinned contact line (Figure 5c shows an intermediate value) until the advancing contact angle ($\theta_A \approx 168°$) of the rough field is reached. The droplet then advances (Figures 5d–f) at constant angle. These behaviors shown in Figures 4 and 5 are consistent with the quantitative data shown in the tables above and inconsistent with the Wenzel and Cassie theories.

Conclusion and Comments

All of the data presented in this paper indicate that contact angle behavior (advancing, receding, and hysteresis) is determined by interactions of the liquid and the solid at the three-phase contact line alone and that the interfacial area within the contact perimeter is irrelevant. This convincingly supports and augments the work of Bartell and Extrand and questions the relevance of Wenzel and Cassie. We do not advocate never using Wenzel's or Cassie's equations, but they should be used with the knowledge of their faults. They support the incorrect concepts that contact area is important and that interfacial free energies dictate wettability. We have not emphasized hysteresis in this paper because we recently explained this phenomenon in detail.[23] Wettability (advancing and receding contact angles, and thus hysteresis) is a function of the activation energies that must be overcome in order for contact lines to move from one metastable state to another. Contact areas play no role in this. Wenzel's and Cassie's equations are valid only to the extent that the structure of the contact area reflects the ground-state energies of contact lines and the transition states between them.