

There are particles in my whiskey!

(The science of whiskey colloids)



Stuart J. Williams

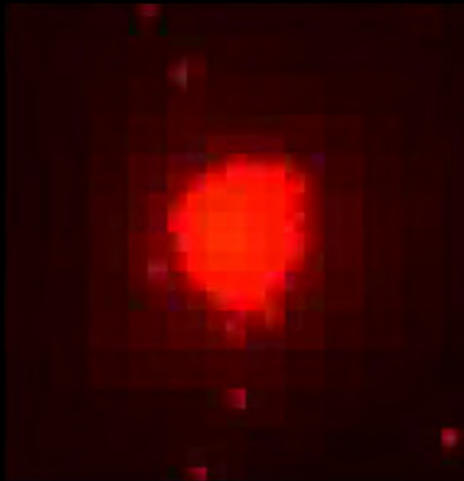
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Mechanical Engineering Dept., University of Louisville

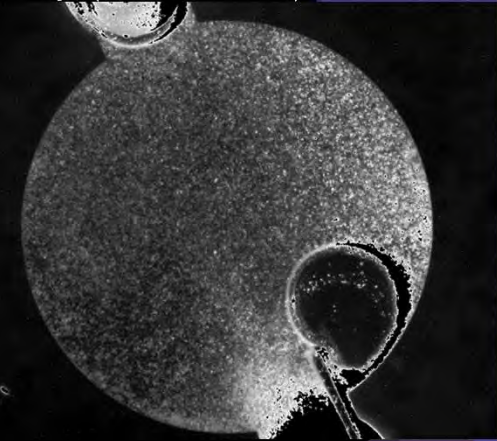
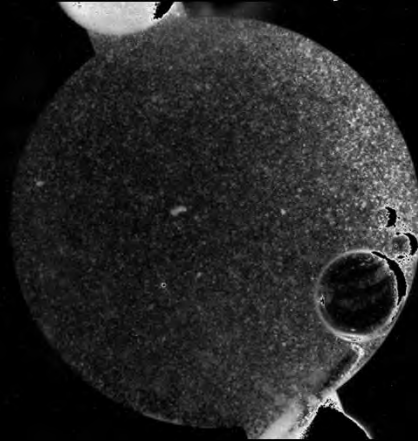


Particles, Fluids, & Visualization

Particle stability in microgravity (NASA, GRC)

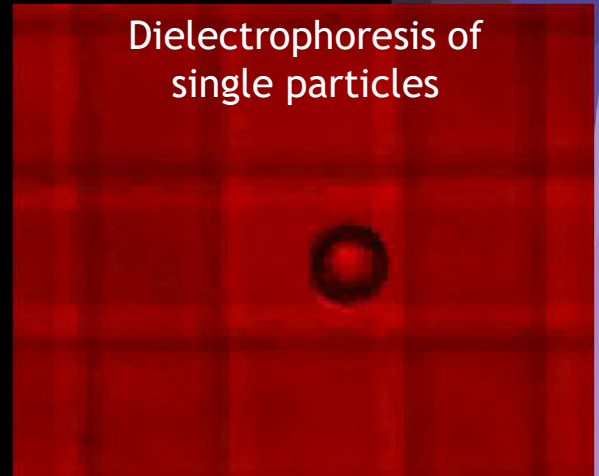


Patterning colloids with optics
and electric fields






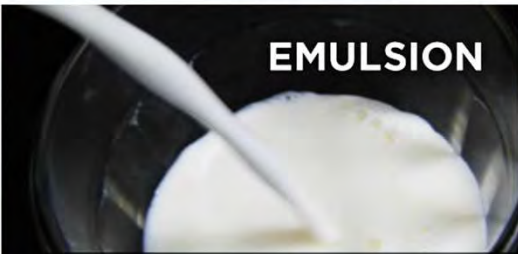




Dielectrophoresis and
electrohydrodynamics

Dielectrophoresis of
single particles



Colloids

PARTICULATE

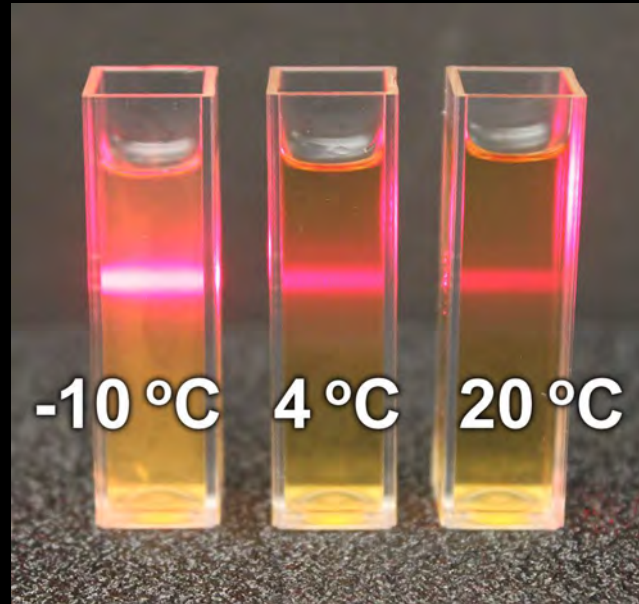
		PARTICULATE		
		GAS	LIQUID	SOLID
BULK CARRIER	GAS	<p>NONE</p> <p>All gases are mutually miscible, so they do not form any sort of colloid.</p>	<p>LIQUID AEROSOLS</p>  <p>Fog, hair sprays, clouds</p>	<p>SOLID AEROSOLS</p>  <p>Smoke, air particulates</p>
	LIQUID	<p>LIQUID FOAM</p>  <p>Whipped cream, shaving cream</p>	<p>EMULSION</p>  <p>Milk, mayonnaise, hand lotion</p>	<p>SOL</p>  <p>Pigmented ink, blood, paint</p>
	SOLID	<p>SOLID FOAM</p>  <p>Styrofoam, pumice</p>	<p>GEL</p>  <p>Gelatin, jelly</p>	<p>SOLID SOL</p>  <p>Cranberry glass</p>

Source: Wikipedia

Outline



1. Introduction
to bourbon



2. Whiskey colloids



3. Whiskey webs

Whiskey Production

Malting - Mashing - Fermentation - Distilling - Maturation

whisky.com

- ▶ Malting: warm, damp environment
- ▶ Germination
 - ▶ Enzymes to convert starch to sugar
- ▶ Kilning (drying)
- ▶ Steeping (moisture)

Not all whiskey grains undergo malting.
For example, corn is typically not malted.



Whiskey Production

Malting - **Mashing** - Fermentation - Distilling - Maturation

American Distilling Institute

- ▶ Grains are ground
- ▶ Hot water activates enzymes
 - ▶ 60 to 65 °C

“Mash bill”

List and proportions of grains used;
typically from corn, wheat, rye, barley

Jim Beam: 77% corn, 13% rye, 10% malted barley

Maker's Mark: 70% corn, 14% malted barley, 16% wheat

Buffalo Trace: 90% corn, 10% rye

Jeptha Creed: 70% bloody butcher corn,
15% malted rye, 10% malted wheat, 5% malted barley



Whiskey Production

Historical importance of limestone water

- ▶ Beneficial minerals (ex: calcium) consumed by yeast
- ▶ Filters particulates, including iron
- ▶ Elevate pH levels
- ▶ Abundant in Kentucky

Some distilleries use natural water resources, others filter city water

Geocaching.com



Whiskey Production

Malting - Mashing - **Fermentation** - Distilling - Maturation

whisky.com

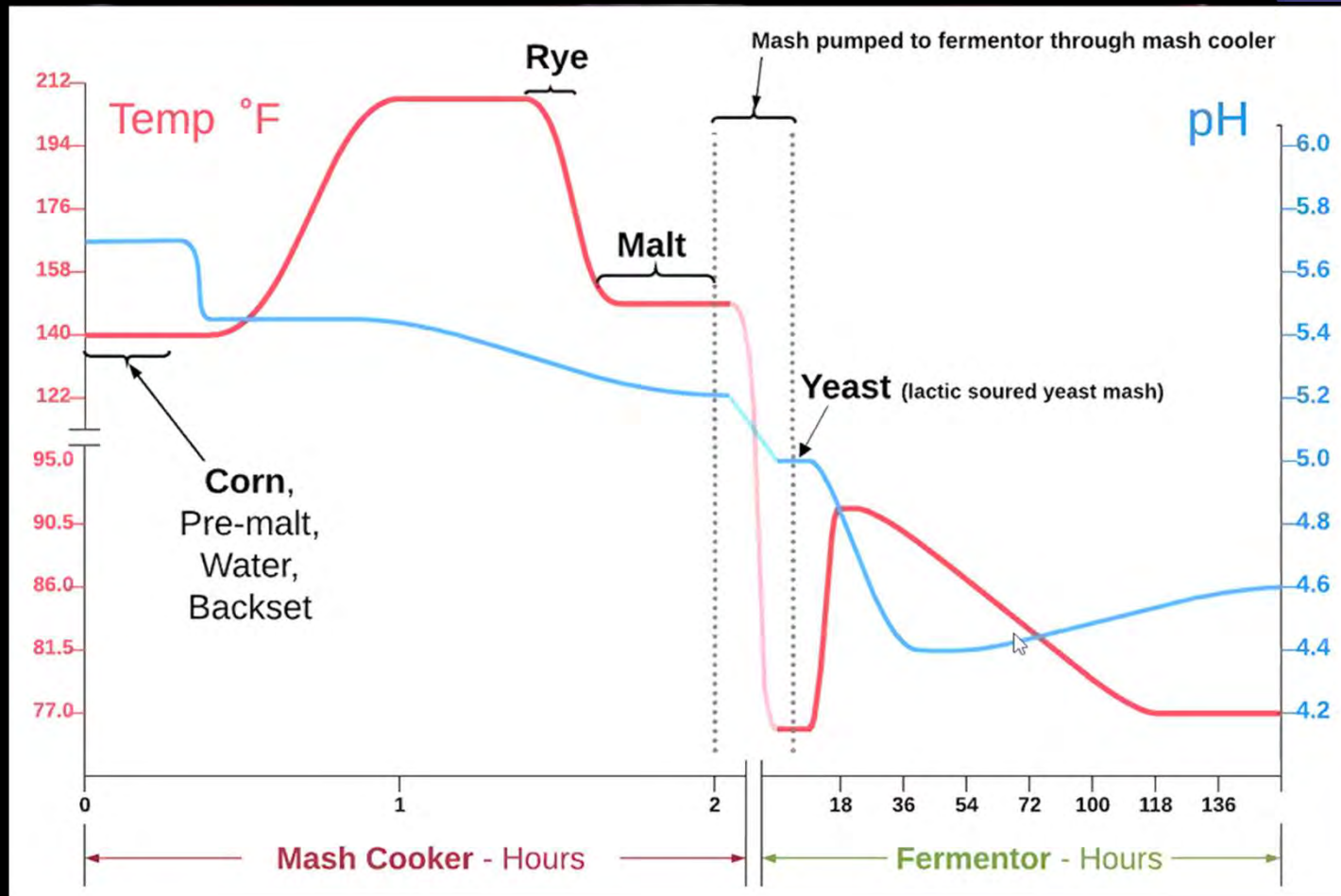
- ▶ Cooled and yeast added
 - ▶ 25 to 30 °C
- ▶ Distillers *carefully* monitor their yeast strains

Four Roses offers ten bourbons using two different mash bills and five different yeast strains



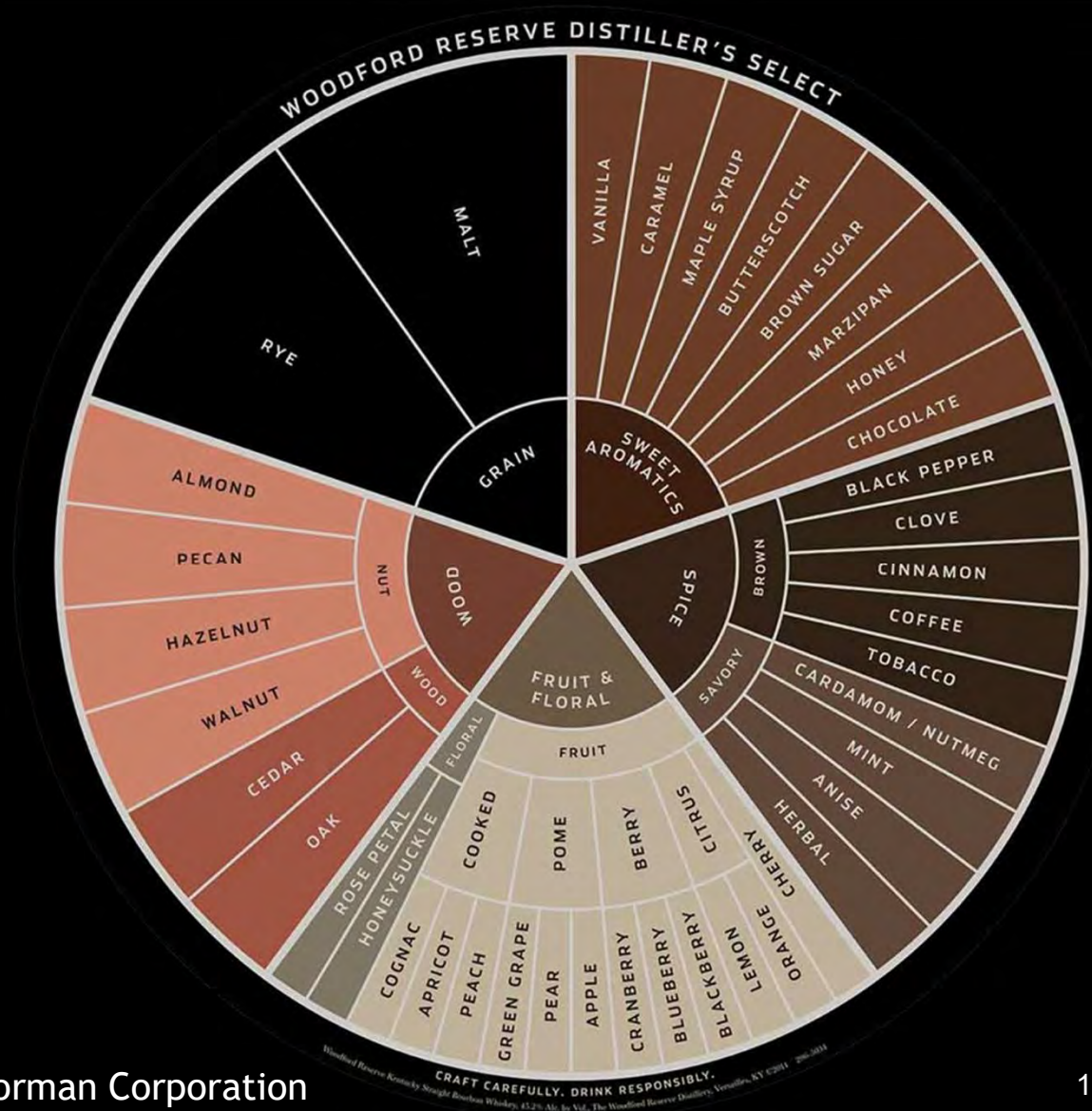
Whiskey Production

Brown-Forman Corporation



Whiskey Production

- ▶ “Flavor wheel”
- ▶ **Congeners** come from each stage of whiskey production
 - ▶ chemical constituent that gives a distinctive character to a liquor
 - ▶ Many are water insoluble



Brown-Forman Corporation

Whiskey Production

Malting - Mashing - Fermentation - **Distilling** - Maturation

Woodford Reserve

- ▶ Heated, condensed, collected
- ▶ Typically double or triple distilled
 - ▶ “Low Wine” 125 proof
 - ▶ “High Wine” 135 Proof
- ▶ Pot still or column still (continuous)

“Proof” = 2X alcohol-by-volume

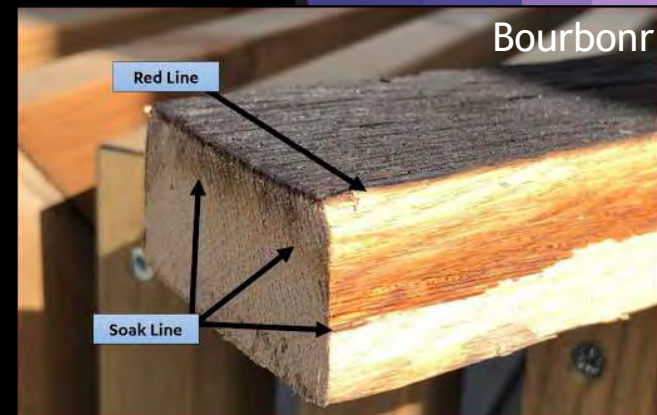


Historic Woodford Reserve pot stills

Whiskey Production

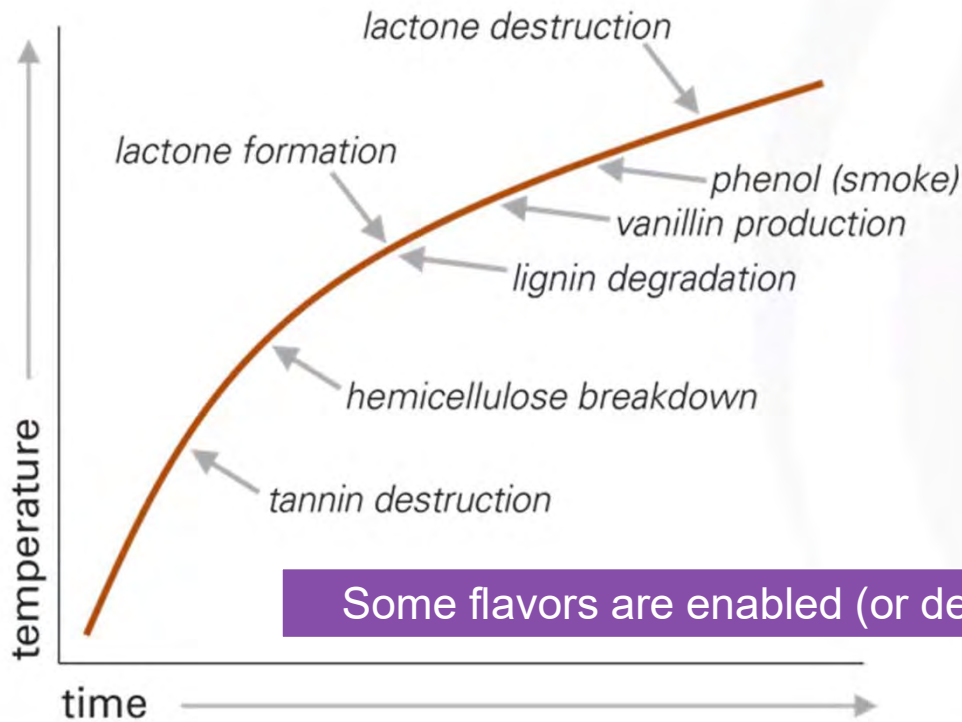
Malting - Mashing - Fermentation - Distilling - **Maturation**

- ▶ Diluted and stored in charred oak barrel
 - ▶ Oak trees: 80+ years old
- ▶ Matured at least four years
- ▶ Evaporation (“angel’s share”) ~ 2% per year

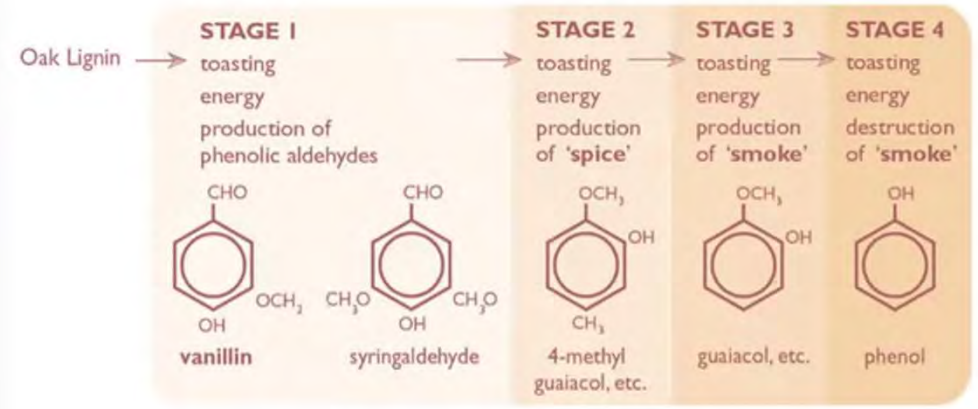


Whiskey Production

Independent Stave Company



Some flavors are enabled (or degraded) as staves are heated.



Some staves are “seasoned” (naturally aged) to increase porosity and bring out other flavors.

FRESH CUT

12 MONTHS

24 MONTHS

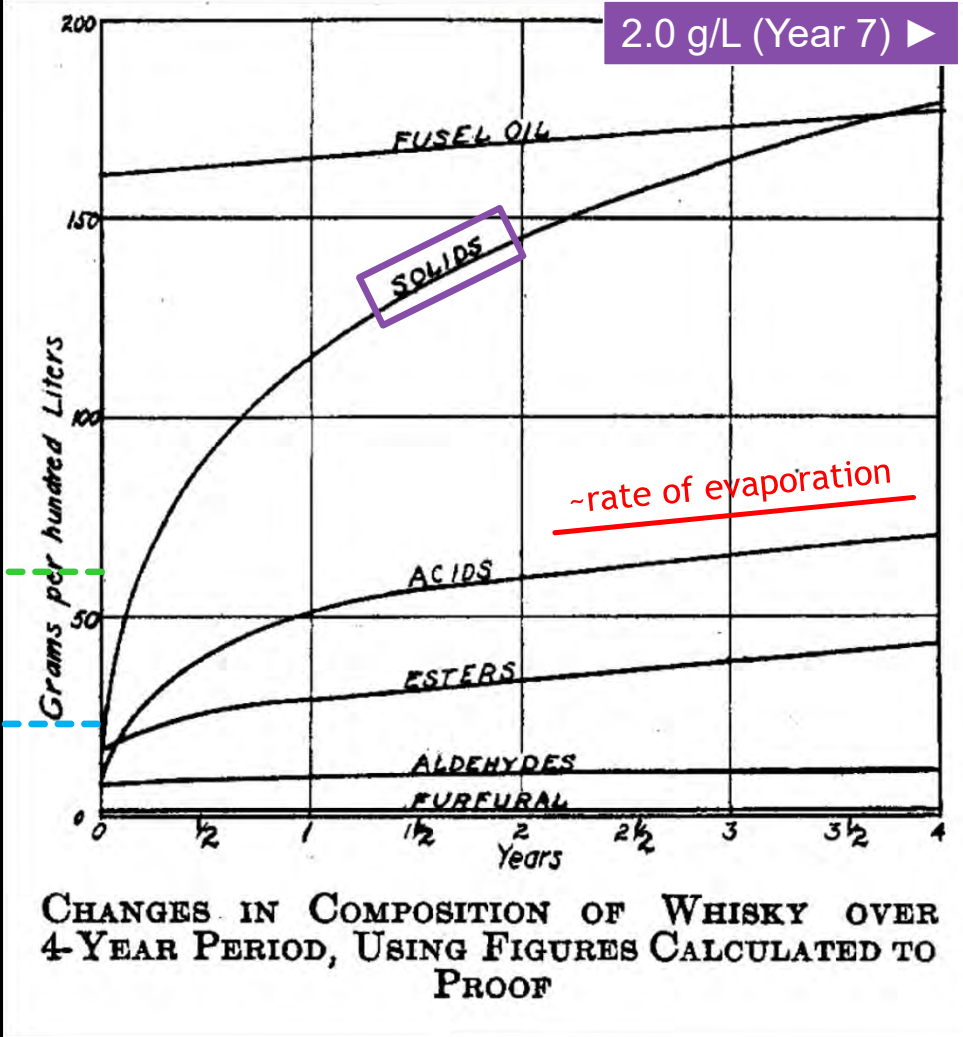
Barrel Aging (Solids)

Bourbon:
1.0 g/L (8 months)
1.5 g/L (27 months)

Distillate:
0.25 g/L

Scotch (unblended):
0.60 g/L (4-8 years)

Charred barrels:
At least *three times* greater water-insoluble content than uncharred or used barrels



“A study of the changes taking place in whiskey stored in wood” Crampton & Tolman, 1907

“Changes in whisky stored for four years” Valaer & Frazier, 1936

“Scotch Whiskey” Valaer, 1940

“Changes in whisky while maturing” Liebmann & Rosenblatt, 1943

Whiskey Production

Techniques to “rapidly” age whiskey

- ▶ Temperature control (Brown-Forman)
- ▶ Ocean barges (Jefferson’s Ocean)
- ▶ Sonic aging (Quadrant)
- ▶ Cavitation (Cleveland Whiskey)



Glyph
(Endless West)
“molecular whiskey”



Bourbon Whiskey:

- ▶ Mash must contain at least 51% corn
- ▶ Distilled at 160 proof or less
- ▶ Put into barrel at 125 proof or less
- ▶ Contain no additives
- ▶ Aged in a new charred oak barrel
 - ▶ New charred barrel-aged whiskey = “American whiskey”

Kentucky bourbon industry (2017 data):

- ▶ 52 distilleries (2016, tripled since 2009)
- ▶ \$8.5B economic output
- ▶ 15k-17k jobs (+2k past two years)
- ▶ \$1.2B building boom



Brown-Forman facility,
by Luke Sharrett of *The New York Times*

Bourbon inventory (2015):

6.7 million barrels

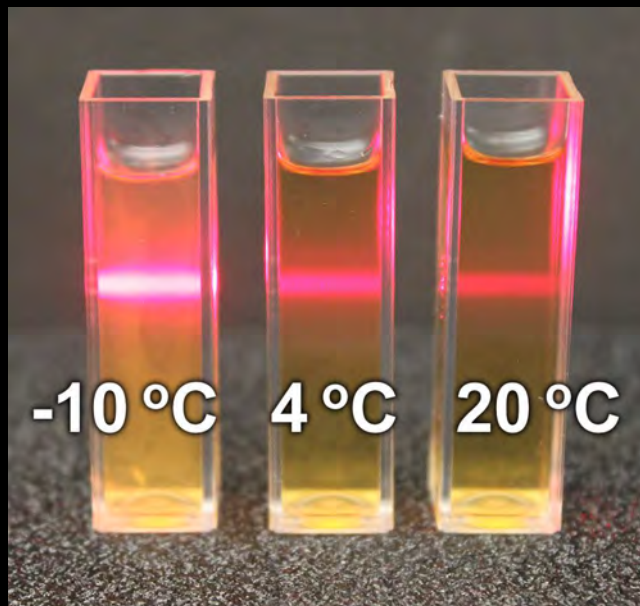
Population of Kentucky:

4.4 million

Outline



1. Introduction to bourbon



2. Whiskey colloids



3. Whiskey webs

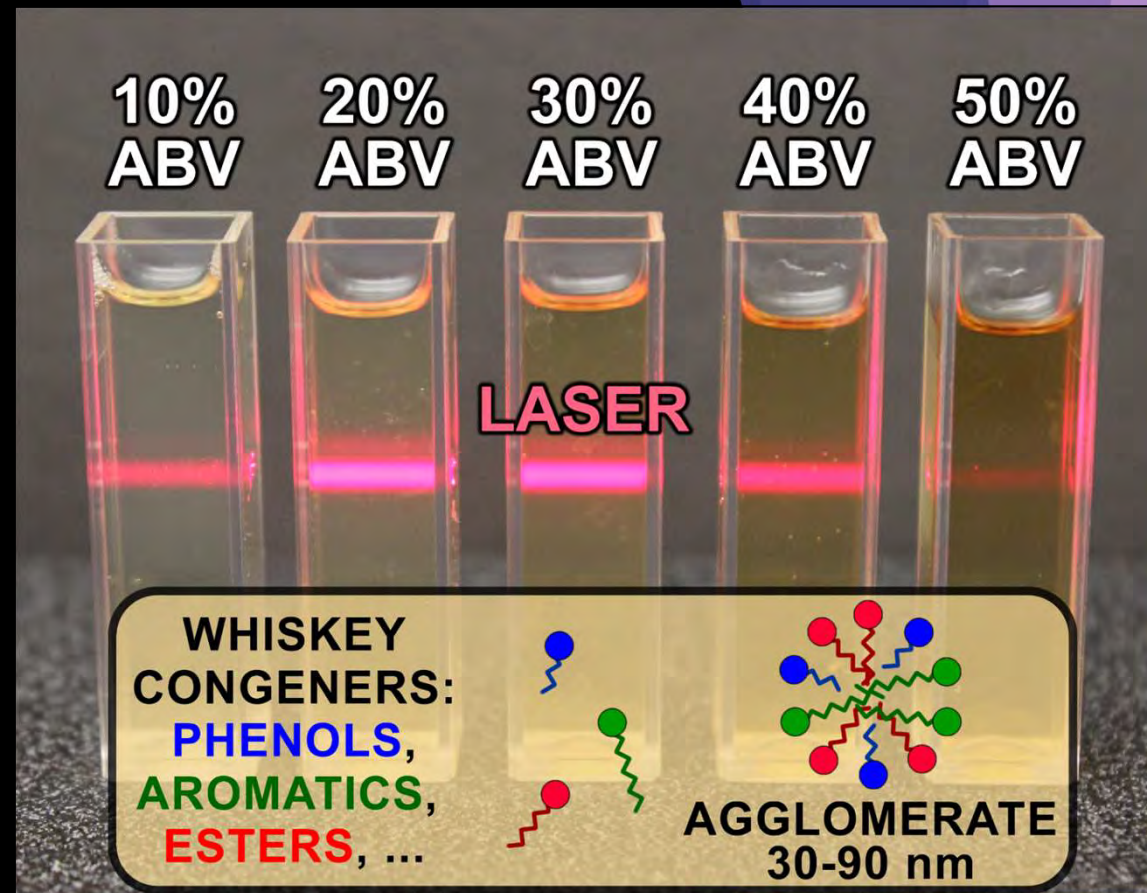
Bourbon Colloids

End product is typically diluted

- ▶ No less than 86 proof

Filtration:

- ▶ Activated charcoal (porous carbon)
- ▶ Chill filtration (some labels “NCF”)
- ▶ **Impacts flavor and color!**



Scattered light: Tyndall effect

Impacts color, flavor, and product stability!

- ▶ Product stability is important to industry
- ▶ Currently no universal, quantifiable technique to assess long-term stability...

Whiskey precipitate is sometimes called “floc”



“The whisky haze” by Charnelle Martins

Extracts from wood

β -sitosterol-D-glucoside

β -sitosterol

Stigmasterol

Campesterol

“Beverage Spirits, Distilled”
*Kirk-Othmer Encyclopedia of
Chemical Technology*

Proposition

- ▶ Use Dynamic Light Scattering (DLS)

First steps: Basic characterization

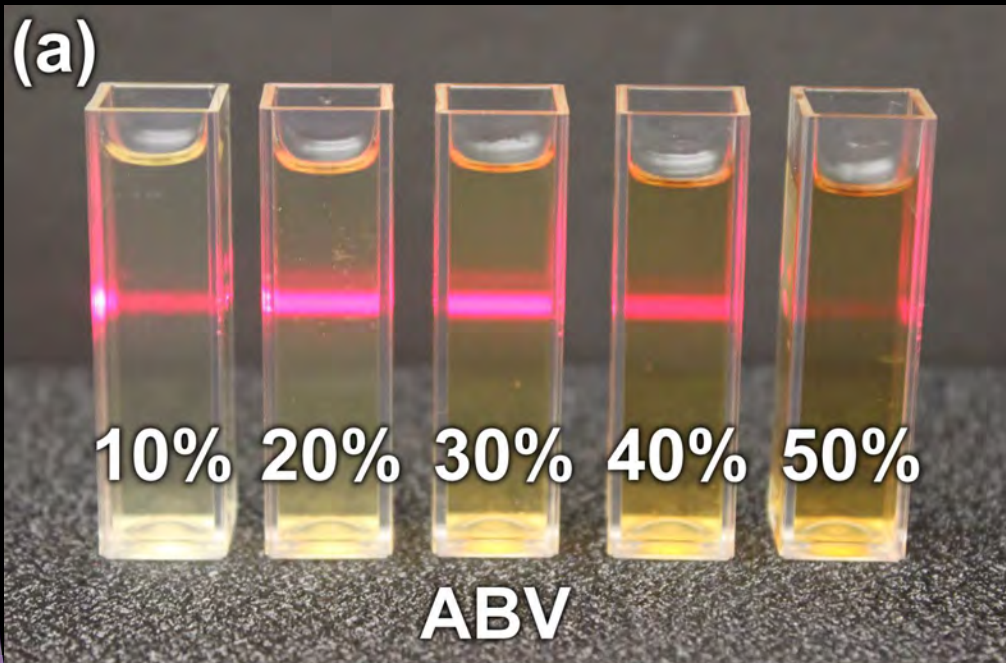
- ▶ Size (Z-Ave)
- ▶ Derived Count Rate (DCR)
- ▶ Polydispersity Index (PDI)
- ▶ Zeta potential (electrophoretic translation)

Tested from 10% to 50% ABV (steps of 5% ABV)
and 0 °C to 40 °C (steps of 10 °C)

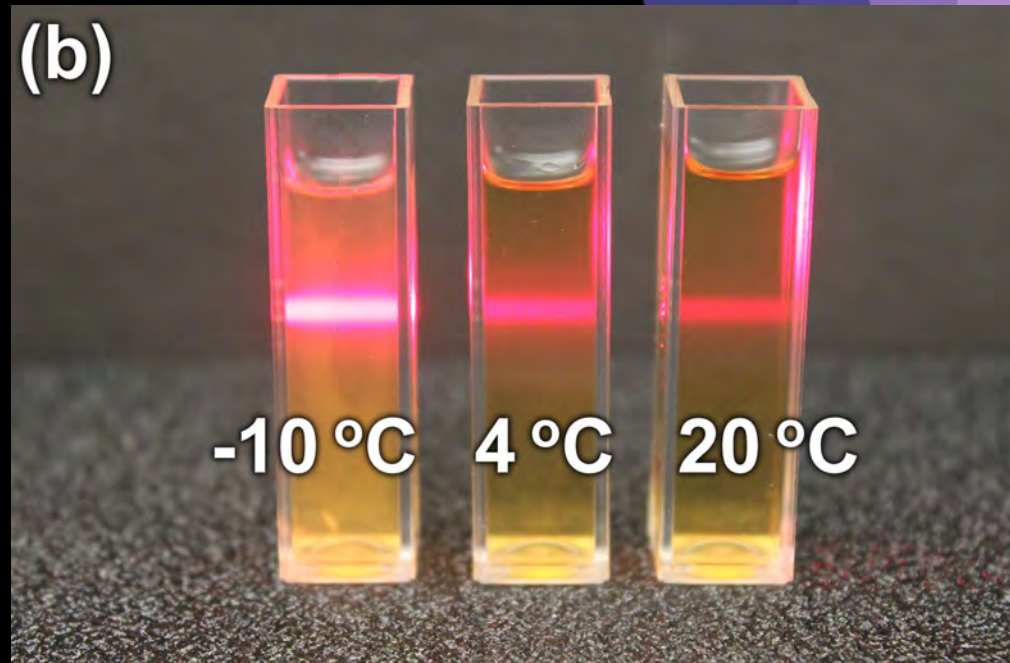


Zetasizer Nano ZSP
Malvern Panalytical

Qualitative Results



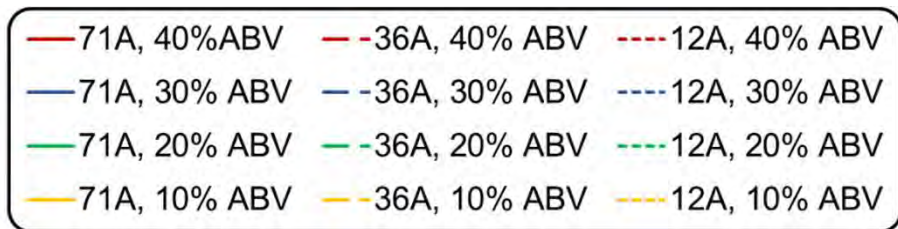
48 month sample, room temperature



48 month sample, 40% ABV

Larger and/or more agglomerates at 20-30% ABV and -10 °C

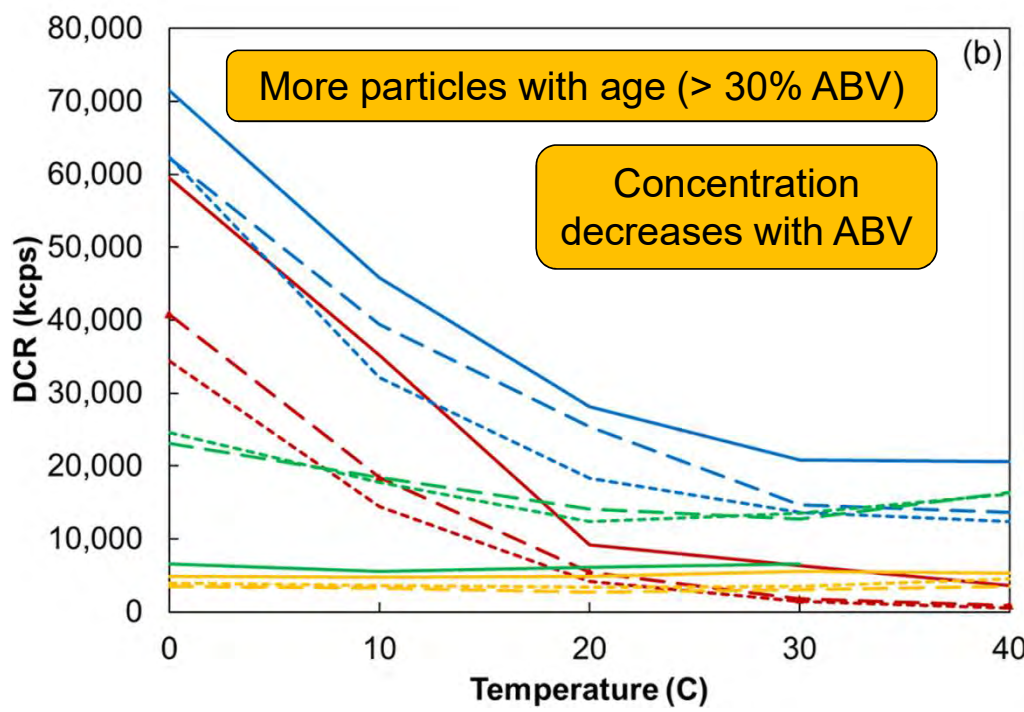
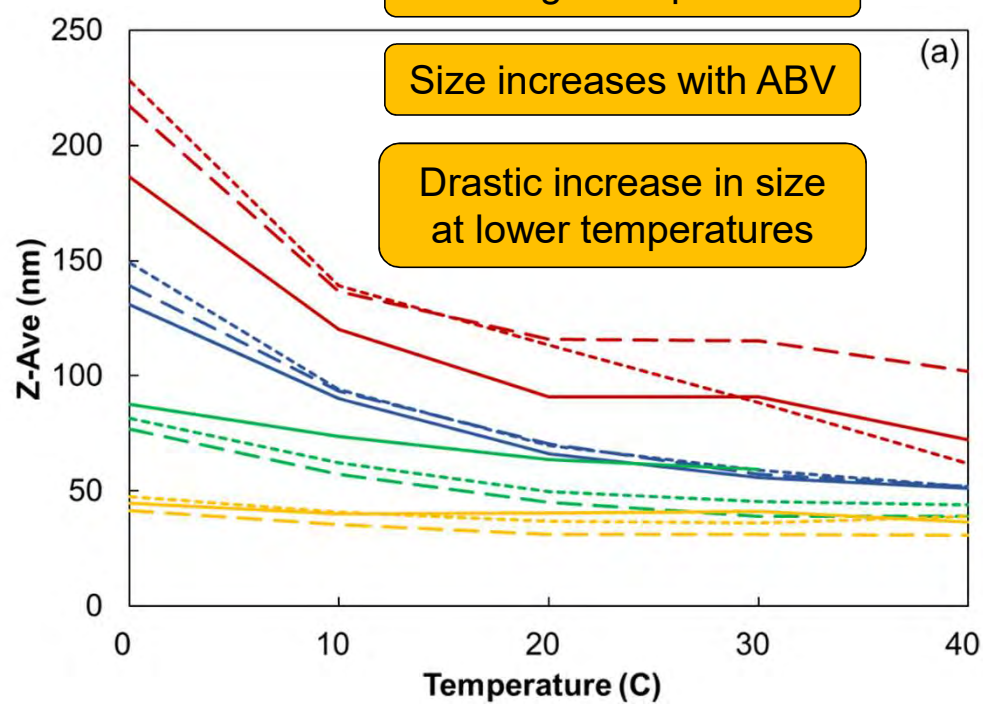
Bourbon Colloids (under review)



Size age independent

Size increases with ABV

Drastic increase in size at lower temperatures



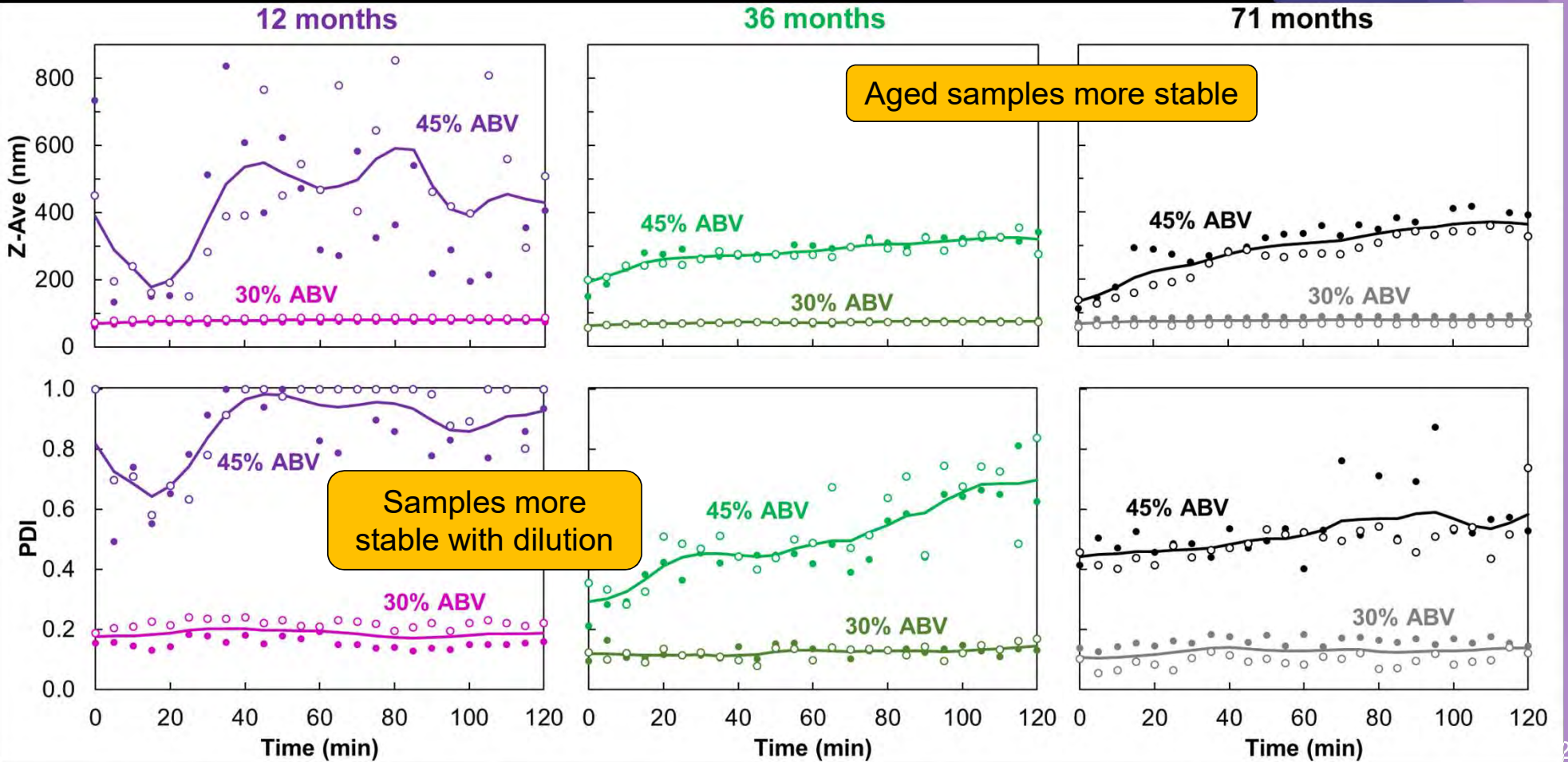
More particles with age (> 30% ABV)

Concentration decreases with ABV

Dilute samples more temperature independent

Bourbon Colloids (under review)

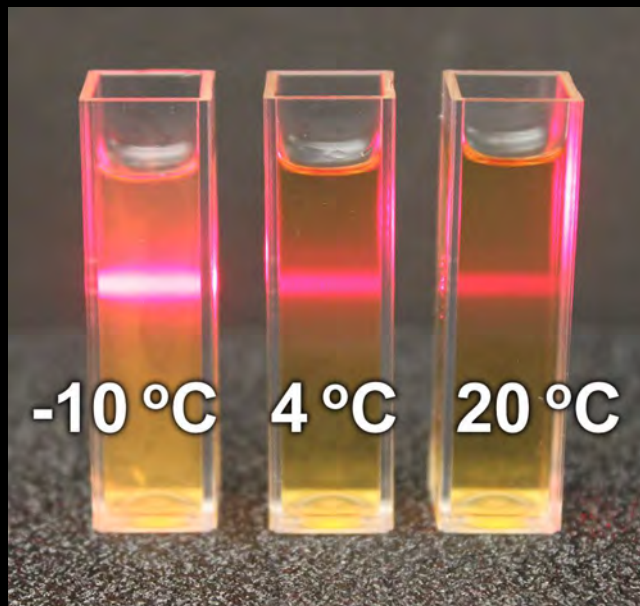
DLS is a straightforward way of providing insight into whiskey colloids for quality control.



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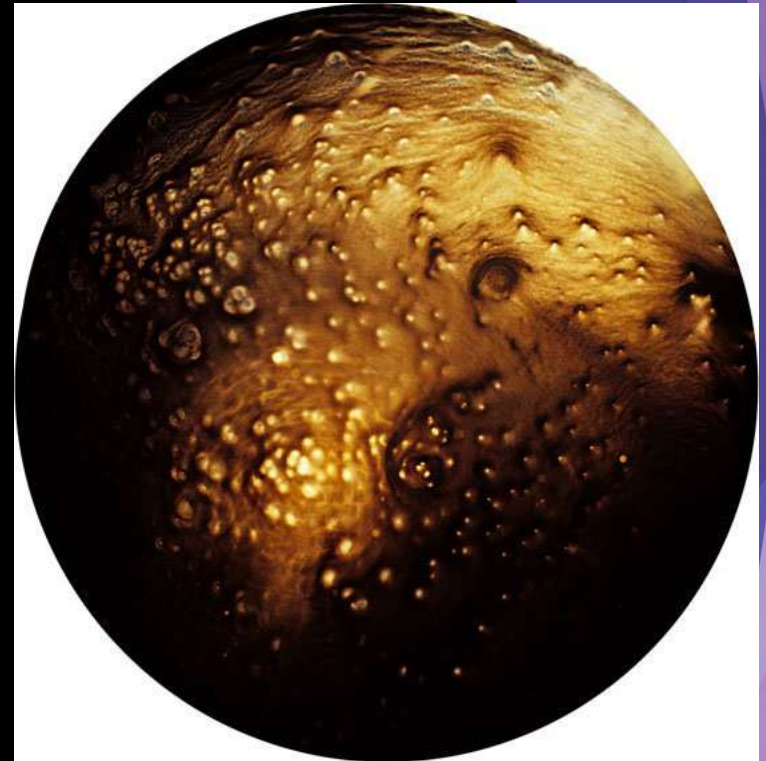


Coffee (Rings) and Whiskey (Films)



Coffee Ring

Image: marketplace.inspirationhut.net



Whiskey Film

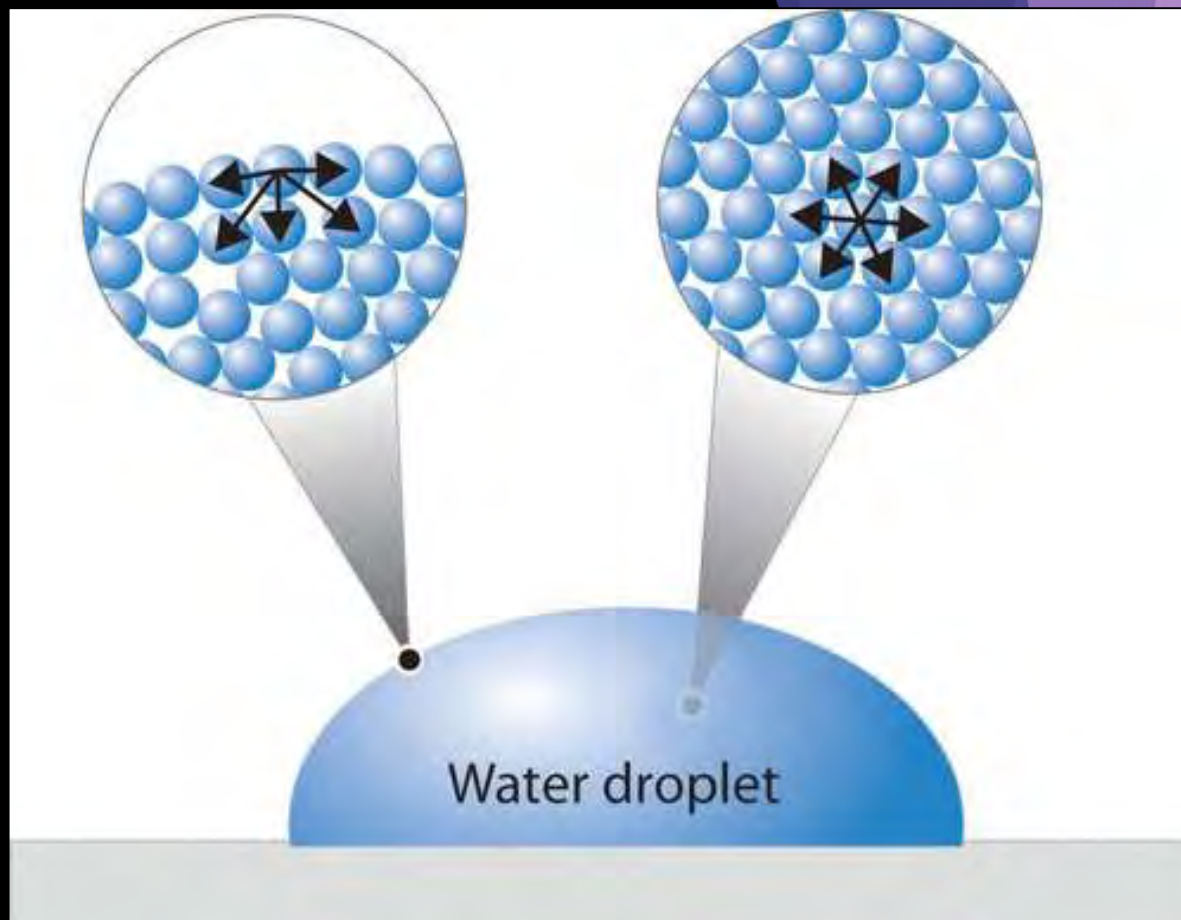
By Ernie Button, "Vanishing Spirits"

Surface Tension

- ▶ Cohesive forces of surface fluid molecules
- ▶ Surfactants lower surface tension

Whiskey:

- ▶ **Surfactants** (fatty acids...)
- ▶ **Polymers** (lignin, polysaccharides, ...)



Petrucci, Ralph H., et al. General Chemistry: Principles and Modern Applications

“Shake the Fake”



“Shake the Fake”

► Samples (same proof)

1. Buffalo Trace White Dog
2. Buffalo Trace
3. Stag Jr.
4. Jameson

► Whiskey aging and filtration impact *fluid* properties

$t \approx 0$

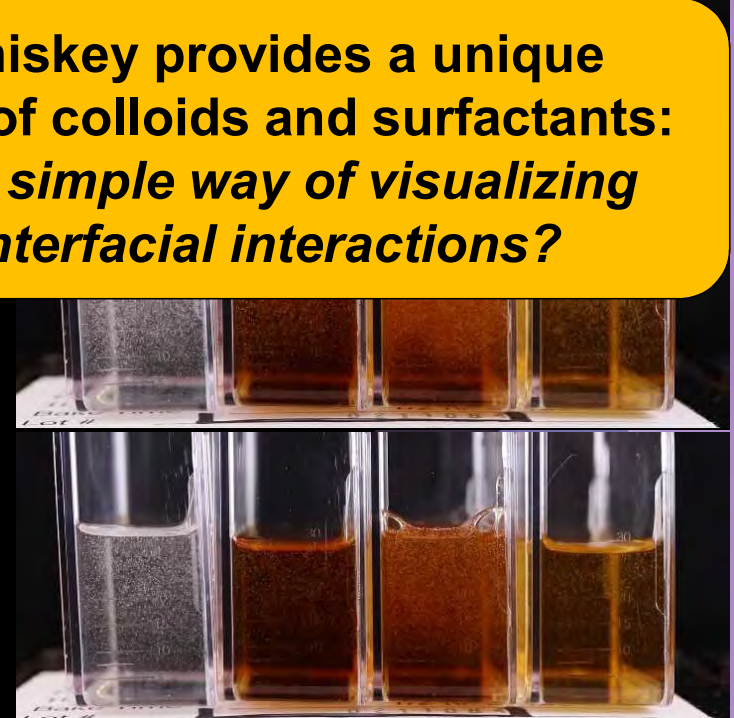


$t = 1 \text{ sec}$



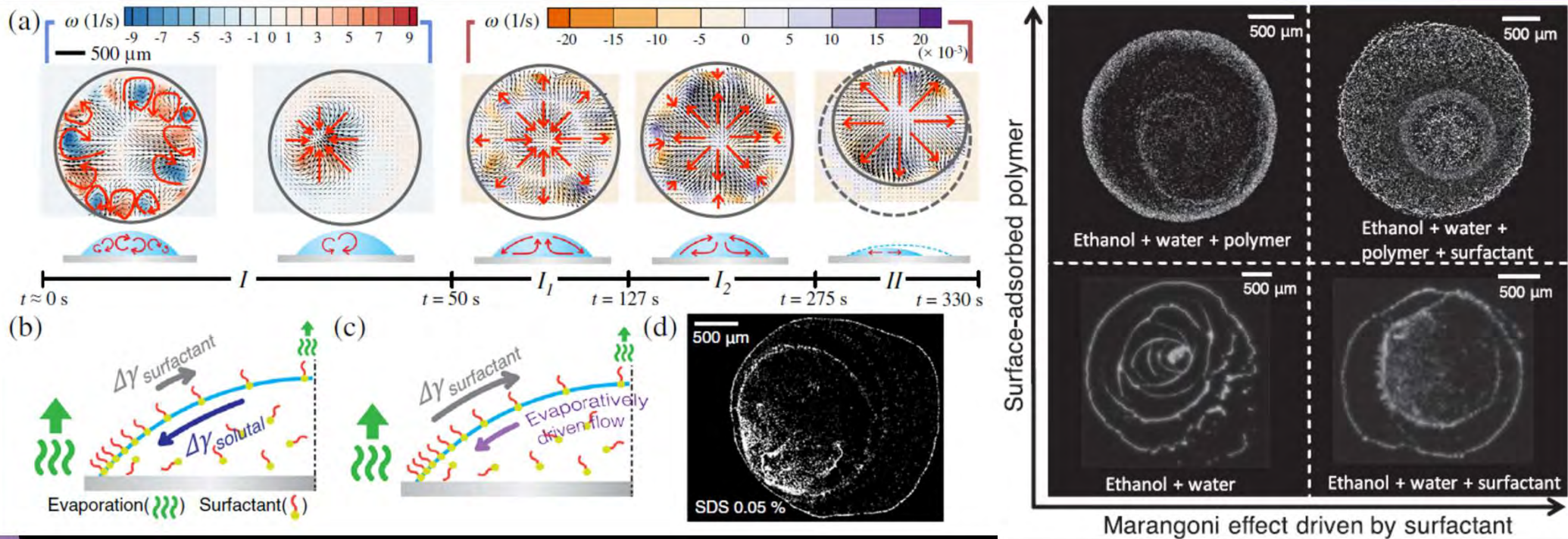
Each whiskey provides a unique “cocktail” of colloids and surfactants:
Is there a simple way of visualizing their interfacial interactions?

$t = 4 \text{ sec}$



Inspired by: JA Davidson, *J Colloid Interface Sci* 81: 540-542 (1981)

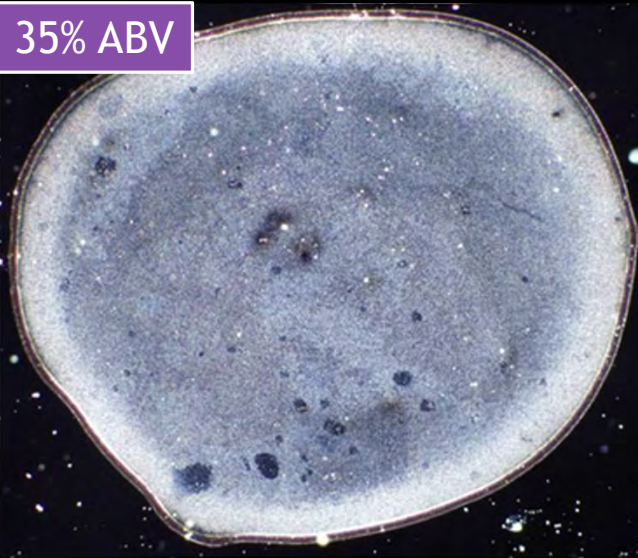
Inspiration



H. Kim, ..., H.A. Stone, *PRL* 116, 124501 (2016)

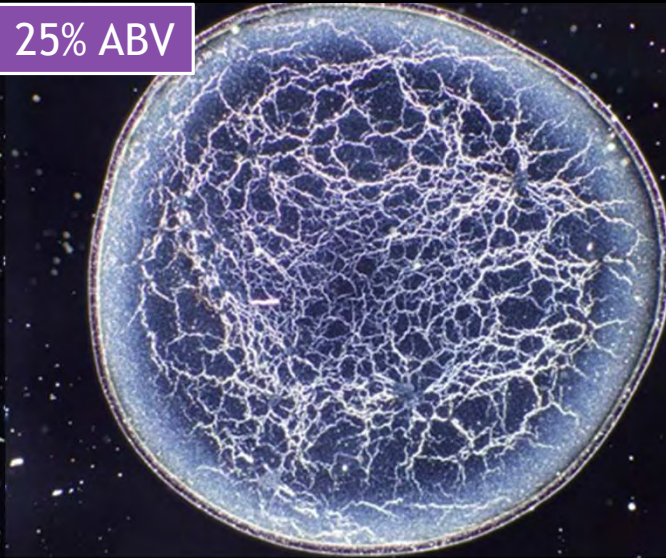
Evaporating a 1.0 μL Drop of Bourbon...

35% ABV



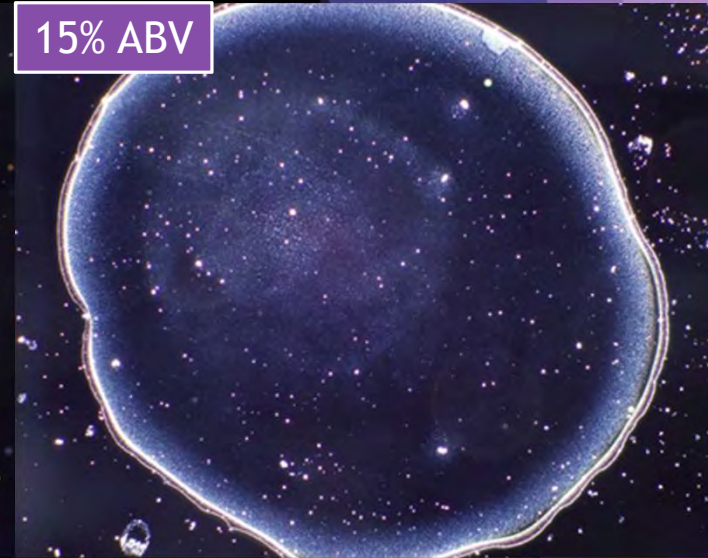
Whiskey Film

25% ABV



Whiskey Web!

15% ABV



“Coffee Ring”

Film ► Web ► Ring

35% ABV

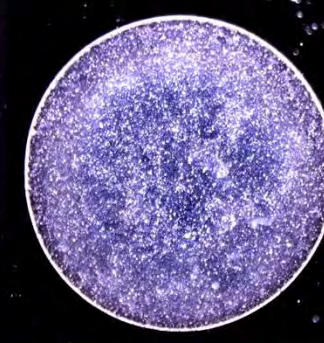
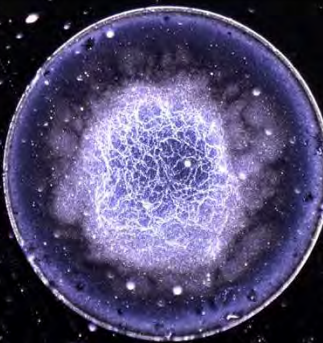
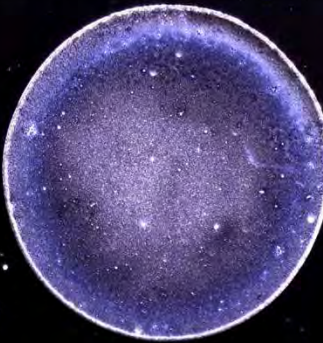
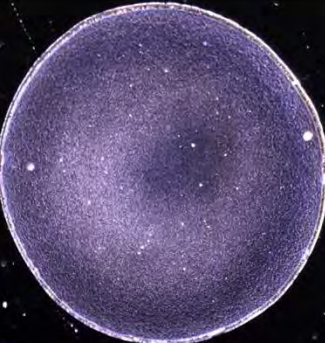
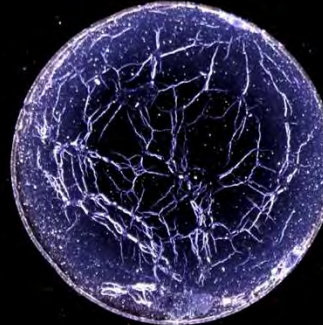
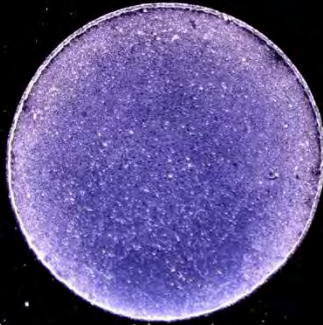
30% ABV

25% ABV

20% ABV

15% ABV

10% ABV

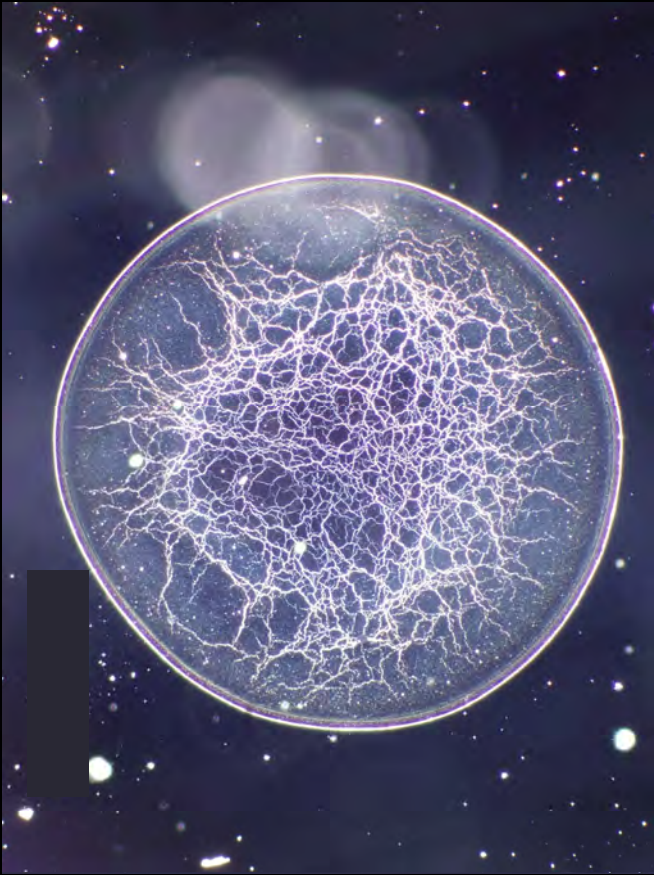


Top row: Rabbit Hole Rye

Bottom row: Pappy Van Winkle, 23 Years

Impact of Surface

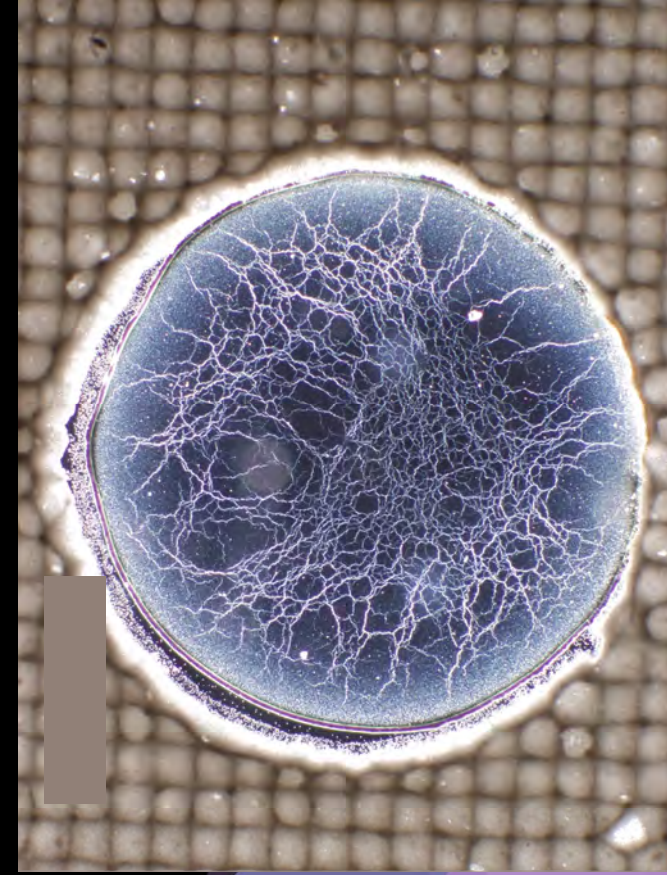
Hydrophobic surfaces are needed to create webs.



Coverslip

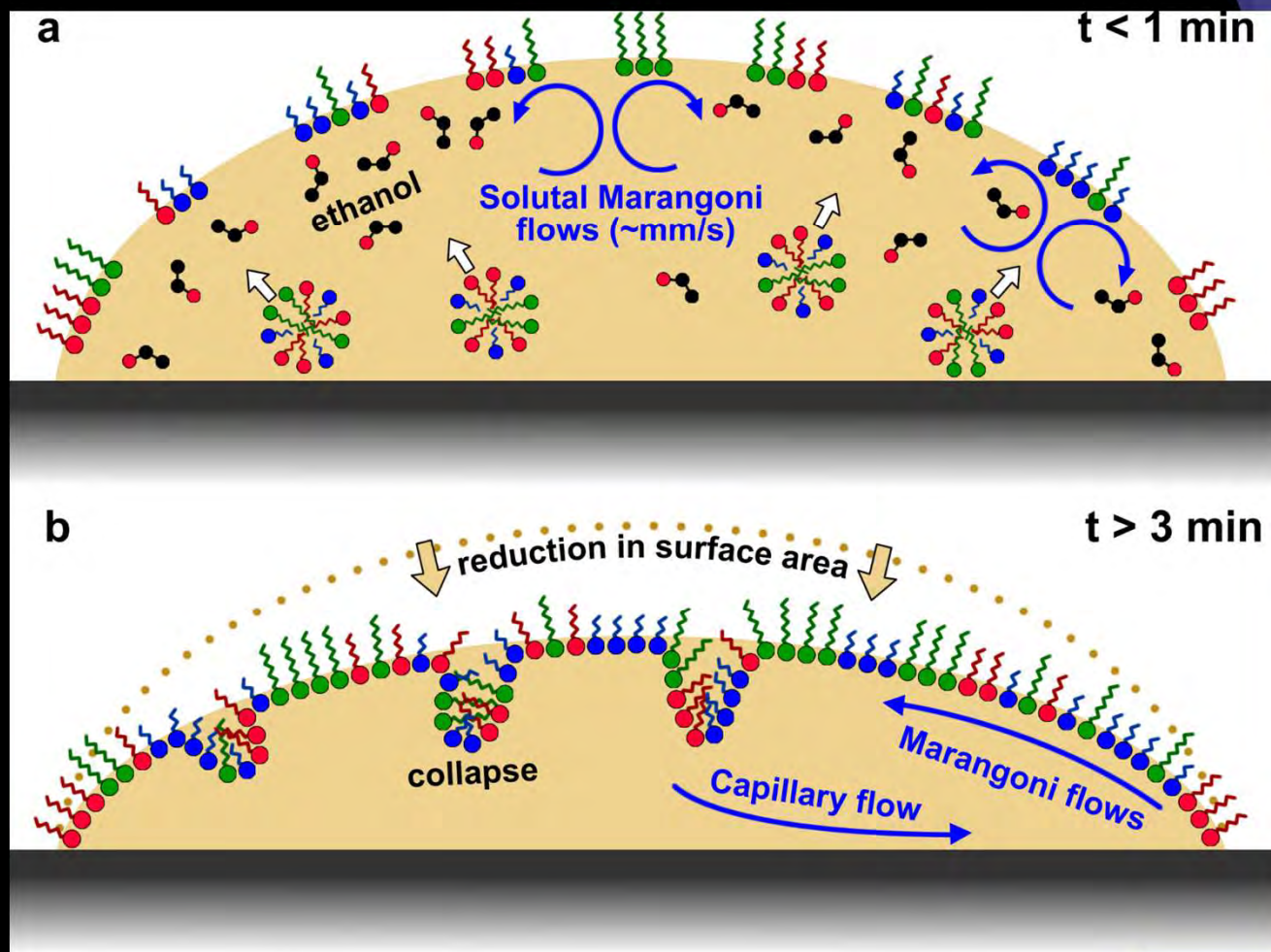


Glass slide



PTFE printed glass slide
(2 mm well)

What's going on?



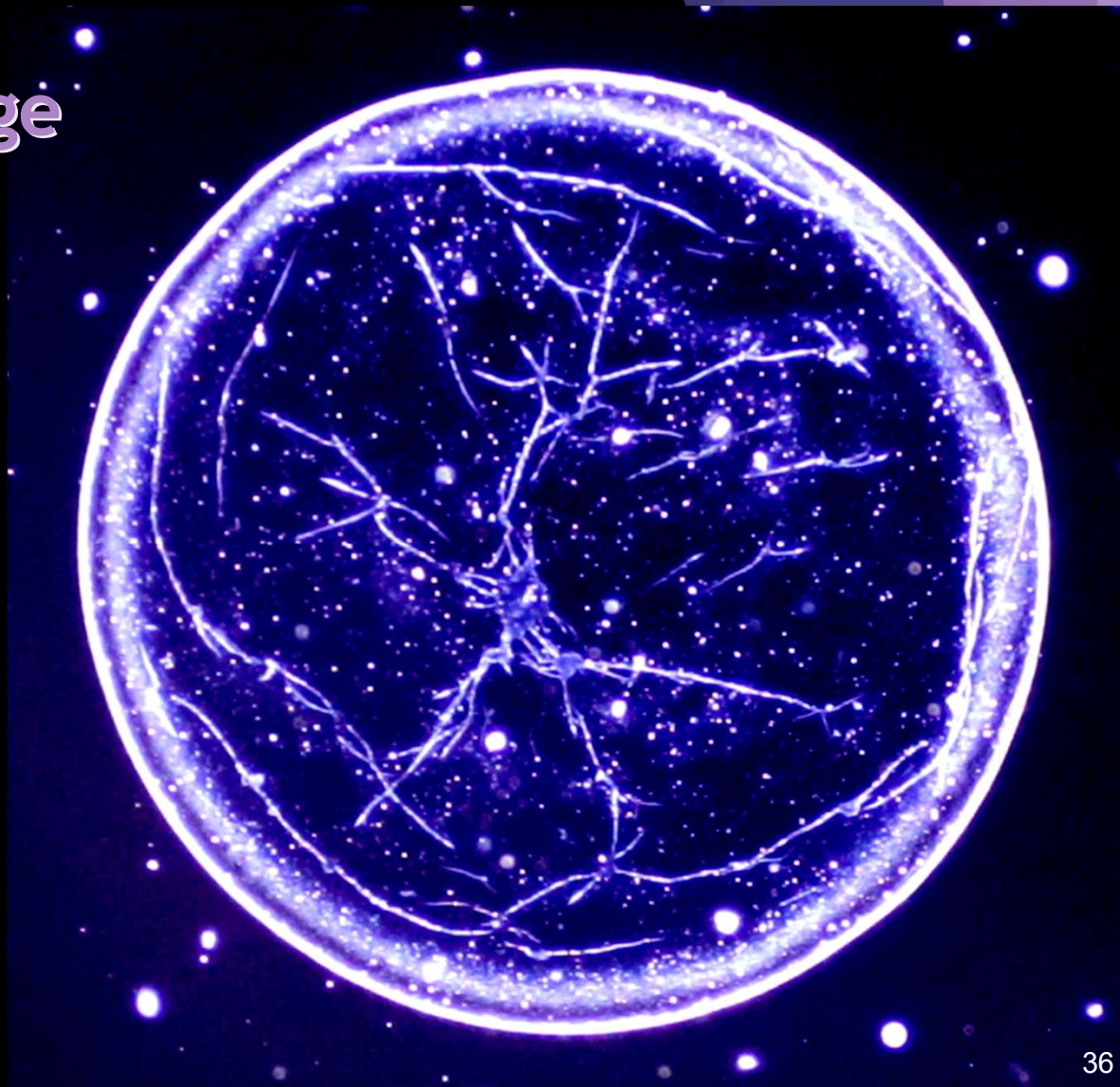
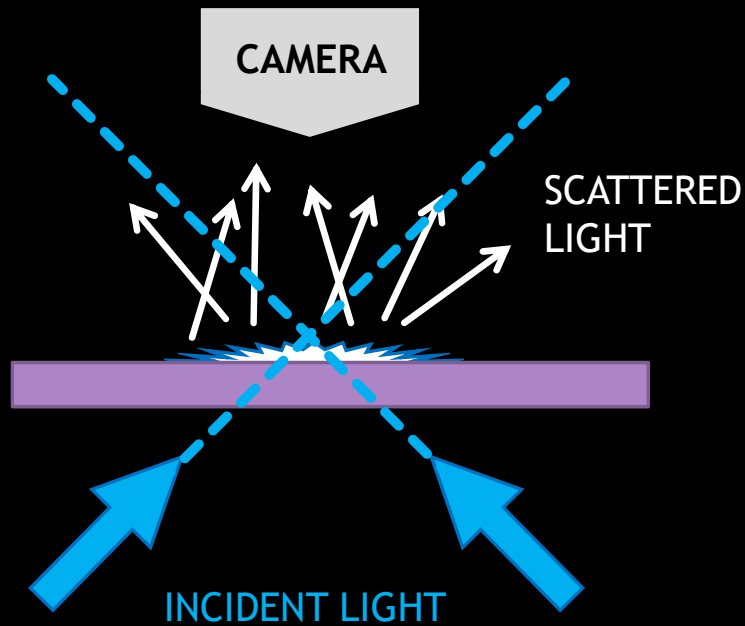
Evaporation: Initial Stage

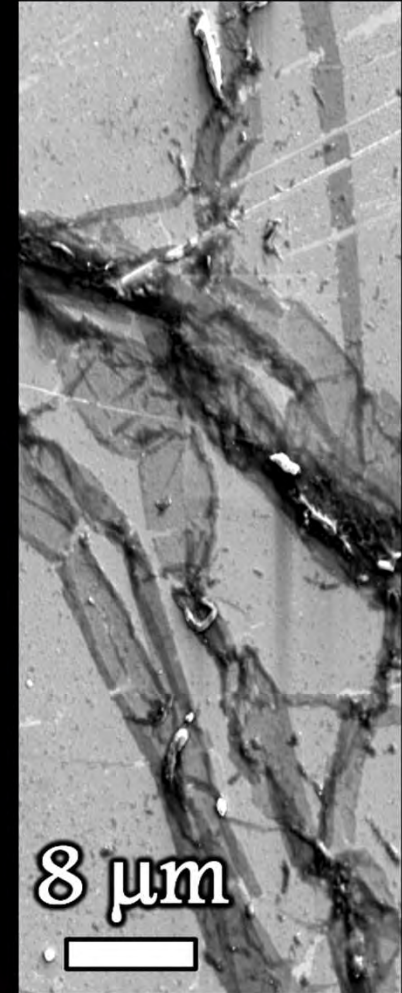
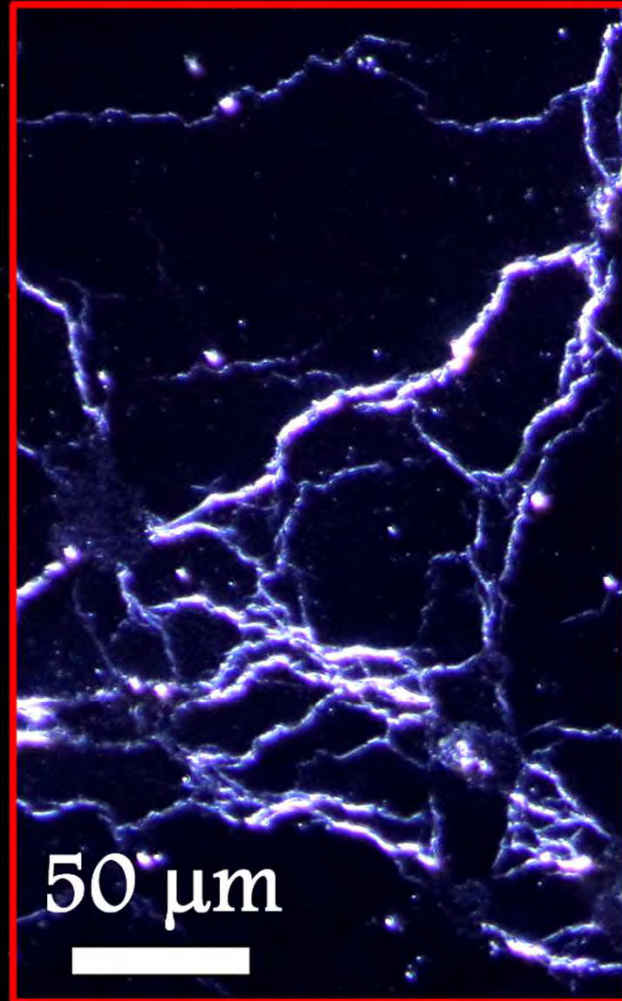
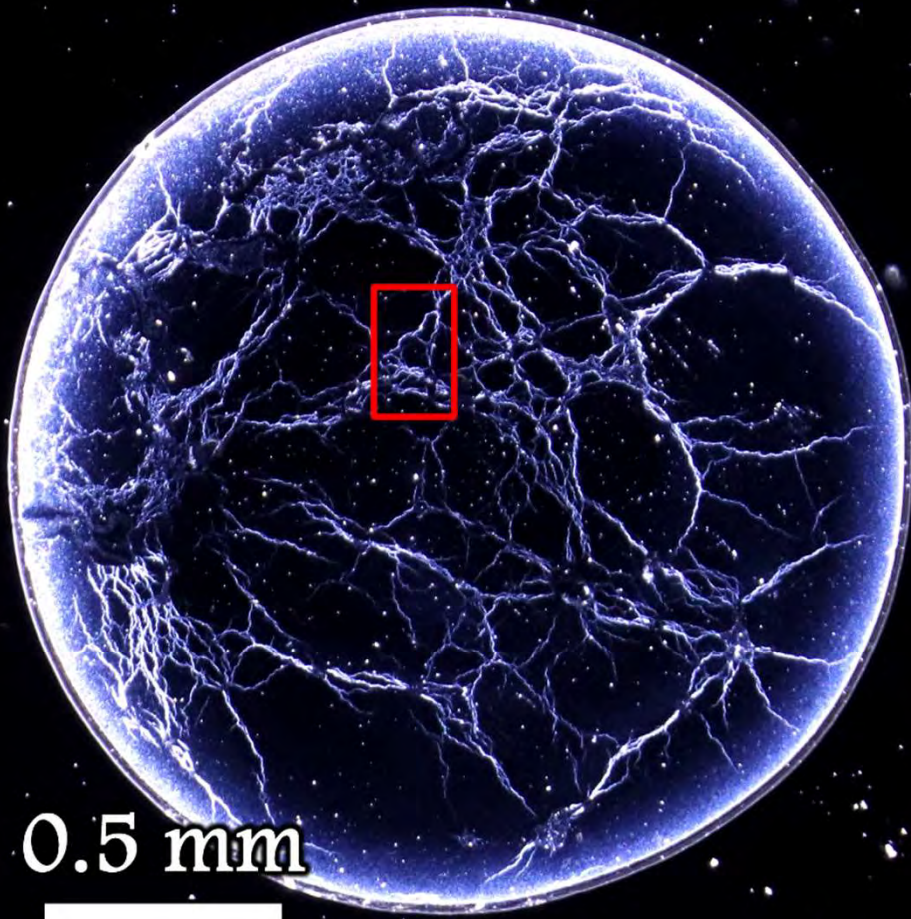
- ▶ Ethanol portion evaporates violently
- ▶ Slows ~ 30 seconds later
- ▶ Responsible for patterning?
- ▶ Tracers added for flow visualization



Evaporation: Final Stage

- ▶ Web structures deposit on surface
- ▶ Imaged: *light scattering*







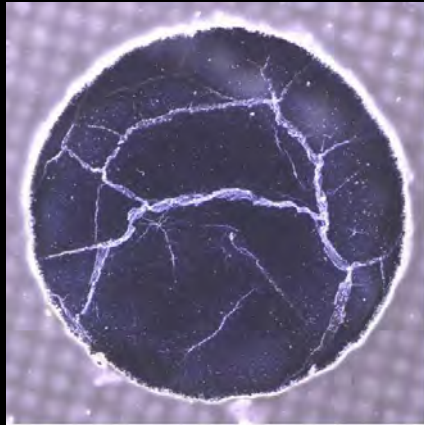
**Every
American
whiskey
is unique!**

- ▶ American whiskey: 65/66
- ▶ Distillate (“white dog”): 0/5
- ▶ Other whiskeys: 0/13
- ▶ Surfactant compromised webs
- ▶ Caramel compromised webs

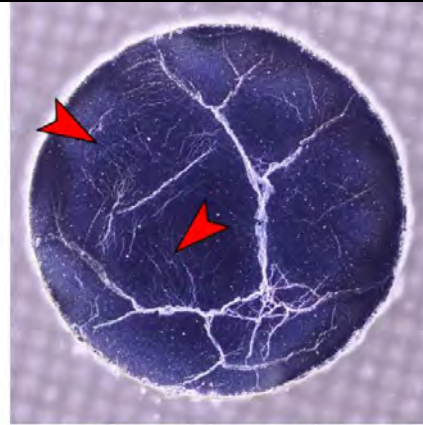
1792 Port Finish	Early Times	Knob Creek	Russell's Reserve Single Barrel
1792 Small Batch	Elijah Craig 23 Year Single Barrel	Knob Creek Cask Strength Rye	Russell's Reserve Small Batch 10 Year
Ardbeg (10 year)	Elmer T. Lee	Maker's Mark Cask Strength	Sazerac Rye 18 Year Old
Baker's Bourbon	Final Reserve (42 years)	Minor Case	Seagram's 7
Beer Barrel Bourbon	Five Fathers Pure Rye Malt Whisky	O.K.I., 10 year	Stagg Jr.
Bernheim Original Wheat Whiskey	Four Roses Single Barrel	O.K.I., 12 year	Thomas H. Handy
Blanton's	George T Stagg	O.K.I., 8 year	Town Branch Bourbon
Booker's	Glen Garioch (12 year)	Old Forester 1920 Prohibition Style	Van Winkle Special Reserve 12 Year
Breckenridge Bourbon Whiskey	Heaven Hill, 6-Year Bottled-in-Bond	Old Forester Birthday Bourbon	W.L. Weller 12 Year
Buffalo Trace	Hennessy	Old Forester Signature	W.L. Weller Special Reserve
Bulleit Bourbon	I.W. Harper	Old Rip Van Winkle 10 Year	Whiskey Row
Canadian Mist	I.W. Harper, 15 year	Old Weller Antique	Wild Turkey Rare Breed
Cleveland Whiskey Black Reserve	Jack Daniel's	Pappy Van Winkle 15 year	Wilderness Trail
Cleveland Whiskey the Eighty Seven	Jack Daniel's, Single Barrel	Pappy Van Winkle 20 Year	William Larue Weller
Collabor&tion, Brandy Finish	Jameson	Pappy Van Winkle 23 Year	Woodford Reserve
Collabor&tion, Mistelle Finish	Jefferson's Chef's Collaboration	Rabbit Hole, Rye*	Woodford Reserve Malt Whiskey
Cooper's Craft*	Jefferson's Ocean Aged	Rabbit Hole, Sherry Cask Bourbon*	Woodford Reserve, Double Oaked
Crown Royal	Jim Beam Single Barrel	Rabbit Hole, Straight Bourbon*	Yellowstone Limited Edition
Deanston	Johnnie Walker (Black Label)	Redbreast (12 year)	Yellowstone Select
Eagle Rare 17 Year Old		Redbreast (21 year)	

Did not form webs (1 μ L, 25% ABV, ambient conditions)

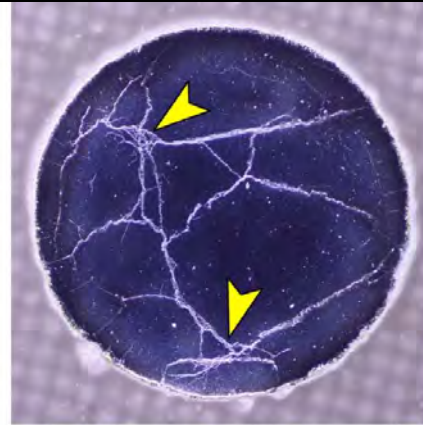
Composition Matters!



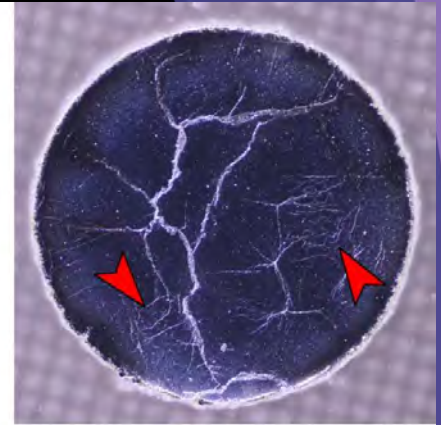
control







acetic acid (400 mg/L)

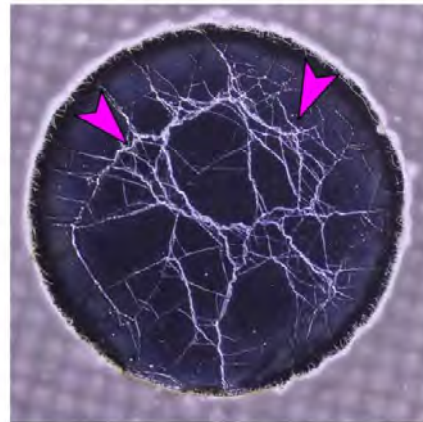


ethyl laurate (700 mg/L)

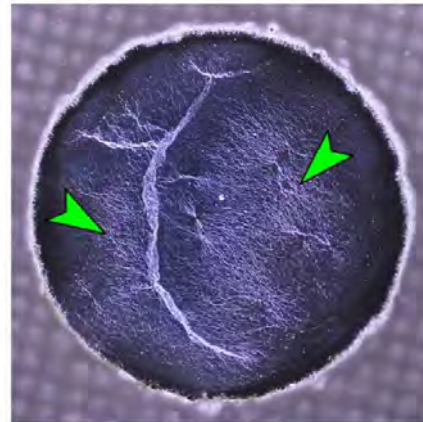


lauric acid (13.5 mg/L)

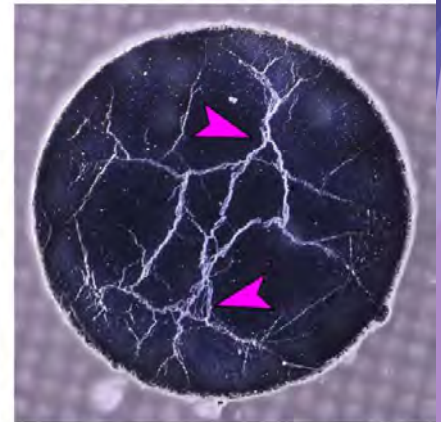
-  more thin strands
-  modified branching
-  increased branching
-  severe wrinkling



lignin (400 mg/L)



tannic acid (450 mg/L)

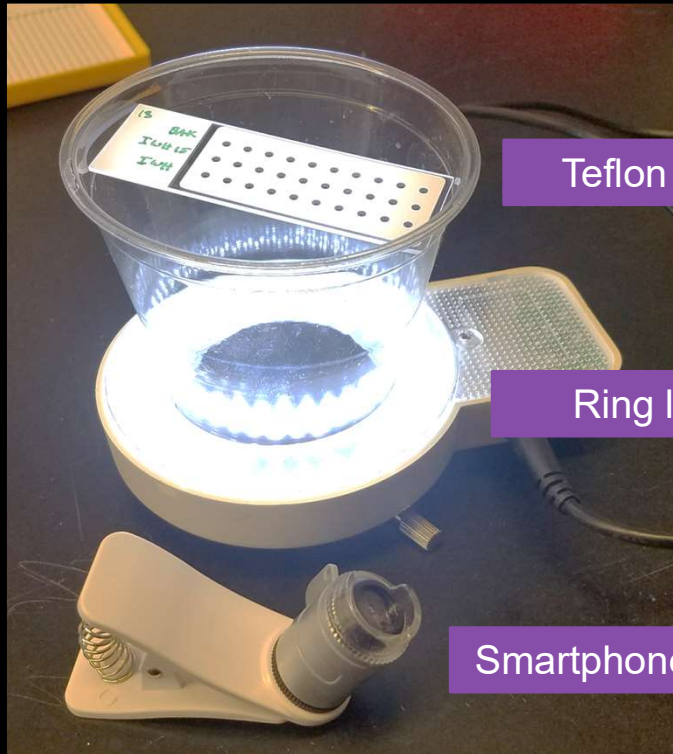


vanillin (4.0 mg/L)

Portable Counterfeit Platform

- ▶ Counterfeit alcohol in the international market
- ▶ Deaths attributed to crude/illicit beverages (ex: methanol)
- ▶ **Portable counterfeit analysis using your smartphone!**

USB microscope cameras work too!

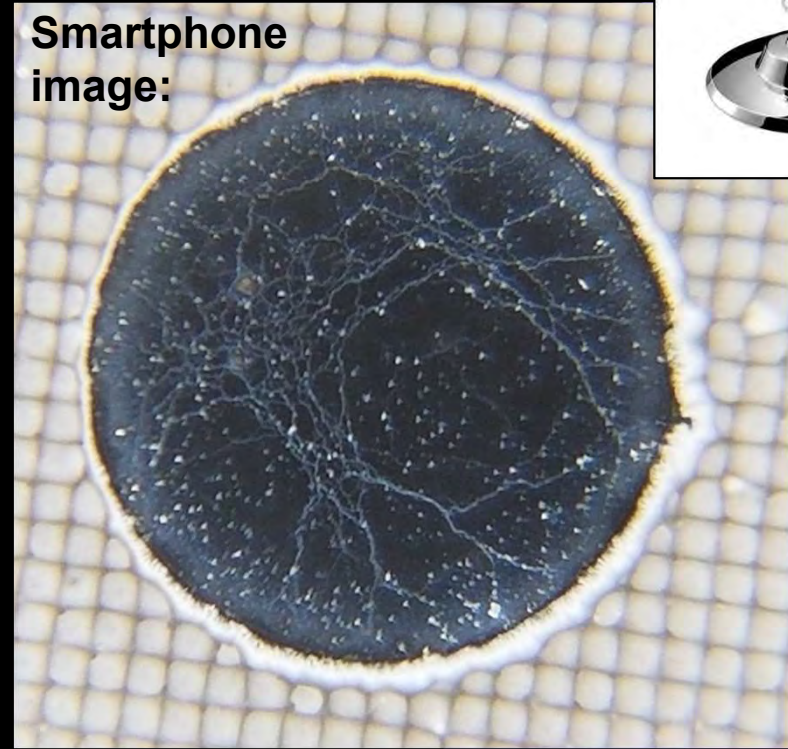


Teflon slide (< \$1)

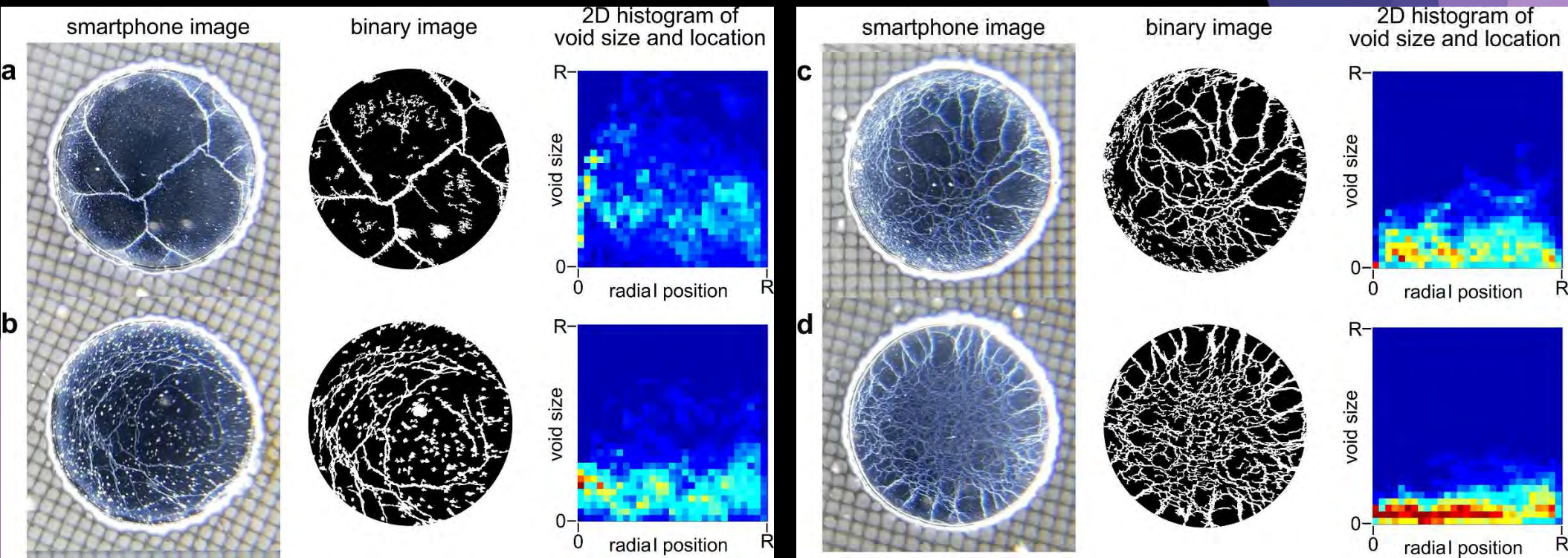
Ring light (\$25)

Smartphone lens (\$6)

Smartphone image:



Smart Phone Analysis



Preliminary digital image study successfully matched "unknown" whiskey to its library image 90% of the time.

Older Samples

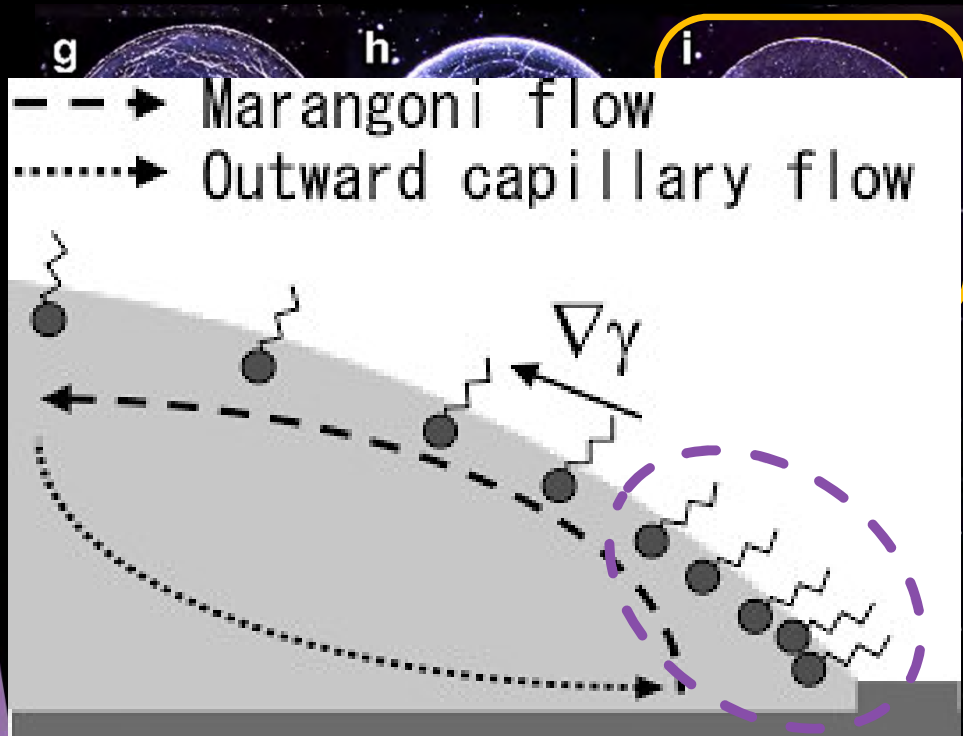


Image Credit: *J. Phys. Chem. B* 2009, 113, 47, 15460–15466



*Final Reserve (42 years) was the only American whiskey that didn't form webs



Why are there no webs at the perimeter?

Pappy Van Winkle 23 year
Secondary market value >\$2000

Future work

- ▶ More robust testing
 - ▶ *Temperature and humidity matter!*
 - ▶ *Sensitive to water source*
- ▶ Quality control investigation
- ▶ Chemically replicate webs
- ▶ Test non-whiskeys & biologically-relevant liquids



AD Carrithers, MJ Brown VI, MZ Rashed, S Islam, OD Velez, and SJ Williams, “Multiscale self-assembly of distinctive weblike structures from evaporated drops of dilute American whiskeys” *ACS Nano*, 14 p. 5417-5425 (2020)

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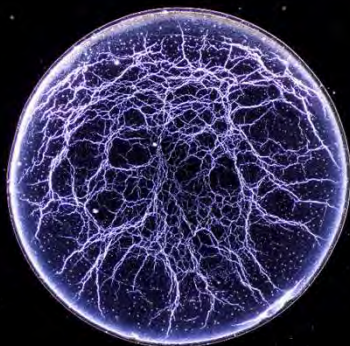
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- ▶ Tom Effler (Brown-Forman)
- ▶ Sabina Islam (NCSU)
- ▶ Orlin Velev (NCSU)
- ▶ Adam Carrithers (UL)
- ▶ Martin Brown (UL)
- ▶ Many others ...



Sabina Islam



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Stuart J. Williams

stuart.williams@louisville.edu

Thank you!



Unfiltered 12 month Brown-Forman sample, 20% ABV