ESI:

Notes on techniques for the study of molecular adsorption at the solid/liquid interface.

This is in response to the question by Prof. Tait about what other experimental methods there are to characterise molecules at the solid/liquid interface other than STM.

Notes by Stuart Clarke (University of Cambridge):

Here are some notes on a variety of methods that can be used to determine particular aspects of molecular species adsorbed from liquids to solid surfaces. In general a combination of these methods is recommended to give a clear picture of these complex and challenging systems. This is not intended as a full review of all the methods one might consider, but a suggestion of some that might be used to complement STM measurements, as prompted by the question raised at the Faraday meeting. I have not included other techniques that colleagues from a UHV background will be familiar with, that should also be employed to characterise surfaces before and/or after adsorption from solution, such as XPS, SIMS, EDX, BSED, FIB-TEM, EELS, EXAFS etc.. which are generally available through national and local services.

In these notes I have included one or two examples drawn from my own experience and papers on hand. In no way do these reflect the extensive body of literature that each of these approaches represents. I hope that interested parties will perform their own review of these techniques that they might be interested to use.

Structural methods

1) *2D – in plane diffraction (Xrays and neutrons):* This approach can be used to determine the in-plane 2D molecular crystal structure of single species and multicomponent combinations. Very high spatial resolution. Xrays and neutrons are ideally combined to address heavy and light components. Powdered substrates used to optimise contribution from the surface (preferential orientation of some substrates can also enhance data collection). A non-invasive approach.

   Extensive body of work including adsorbed alkanes, alcohols, fatty acids, amines, amides, ‘spheres’, ‘dipoles’, ‘quadrupoles’ etc.. hydrogen bonded systems, halogen bonded systems..etc. Temperature dependent studies.

   Usually done as a coverage dependent measurement from sub monolayer (‘dry’) to multilayer systems (‘wet’). Usually only very limited amounts of ‘liquid/bulk’ are possible without obscuring the 2D crystal pattern. (unless there are peaks in a different region of the pattern to the fluid). Hence most work is at submonolayer coverages, but some have gone to study solid layers coexisting with liquid.

   Detailed analysis of the lineshape can give other physical parameters such as 2D domain size, elastic properties and 2D vs 3D nature of the overlayer structure.

   The evolution of the 2D diffraction pattern with composition can indicate the mixing in the 2D solid layers.

   A number of these solid layers (eg halogen bonded co-crystals) have not been seen with STM (despite trials by us and other more experienced STM users!).

Synchrotron Xray sources are preferred over lab-based source for the high flux. Neutrons require a suitable centrallised facility and appropriate access by peer review application.

Examples of Systems:

Alkanes on Graphite:

Espeau, et al, X-Ray diffraction from layers of *n*-alkanes adsorbed on graphite,, DOI:10.1039/A701071K, *J. Chem. Soc., Faraday Trans.*, (1997) **93,** 3201-3208

Diama, et al, Structure and phase transitions of monolayers of intermediate-length n-alkanes on graphite studied by neutron diffraction and molecular dynamics simulation
The Journal of Chemical Physics **131**, 084707 (2009); doi: http://dx.doi.org/10.1063/1.3212095

Castro, et al. *Physical Chemistry Chemical Physics,* **4**, 345-351(2002). 'The Crystalline Structures of the even alkanes hexane, octane, decane, dodecane and tetradecane monolayers adsorbed on Graphite at Submonolayer Coverages and from the Liquid'.

Arnold, et al, *Physical Chemistry Chemical Physics* **4,** 3430-3435 (2002). 'The Crystalline Structures of the odd alkanes pentane, heptane, nonane, undecane and tridecane monolayers adsorbed on Graphite at Submonolayer Coverages and from the Liquid'.

Inaba, et al, *Chemical Physics Letters,* **352,** 57-62 (2002), 'Mixing behaviour in 2D layers of linear alkanes adsorbed on graphite'.

Haloalkanes on graphite:

On graphite: Parker, J. E. and Clarke. S. M., *Langmuir,* **24** 4833 – 4844 (2008), 'Mixing in Adsorbed Monolayers: Perfluorinated Alkanes'. DOI: 10.1021/la703995u.

Parker et al, *J. Phys Chem*., ***C113*** 21396–21405 (2009), 'The Crystal Structure of Monolayers of Fluorinated Alkanes on graphite'.

Morishige, et al, *Molecular Physics*, **72** 395-411 (1991). 'The Structure of Chloromethane Monolayers Adsorbed on Graphite'.

Clarke, et al, *Acta Chimica Hungarica,* **130** 441-449 (1993). 'Close Packing in Two Dimensional Layers: The Structure of cis-1,2 dichloroethene Monolayer on Graphite'.

Sun, et al, *Molecular Physics,* **110** 217-225 (2012). 'The Structure of the 1-Bromononane and 1-bromoheptane Monolayers Adsorbed on the Surface of Graphite'. DOI: 10.1080/00268976.2011.640290.

Bucknall, et al, *Molecular Physics,* **67** 439-446 (1989). 'The Structure of a Methyliodide Monolayer Adsorbed on Graphite'.

Nitrogen on graphite:

Wang, et al, Orientational order in nitrogen monolayers adsorbed on graphite at low temperature, Phys. Rev. **B 35**, 5841.

Carboxylic acids on graphite:

Bickerstaffe, et al, *J. Phys Chem.,* **110** 5570-5575 *(2006)*, 'The Crystalline Structures of Carboxylic Acid Monolayers Adsorbed on Graphite*'*

Castro, et al, *Journal of Physical Chemistry*, **B102** 777-781 (1998). 'A Crystalline Monolayer of Dodecanoic Acid Adsorbed on Graphite from n-Heptane Solution'.

Alcohols on graphite:

K. Morishige and T. Kato, Chain-length dependence of melting of *n*-alcohol monolayers adsorbed on graphite: *n*-hexanol, *n*-heptanol, *n*-octanol, and *n*-nonanol. *The Journal of Chemical Physics* **111**, 7095 (1999); doi: http://dx.doi.org/10.1063/1.480001

S. Clarke, et al, *Applied Physics A*, (2002) **74**, pp s1072–s1073, Linear alcohols adsorbed on graphite from the liquid.

K. Morishige, Structure and melting of a monolayer ethanol film on graphite. *The Journal of Chemical Physics*, **97**, 2084 (1992); doi: http://dx.doi.org/10.1063/1.463146.

Amides on graphite:

Bhinde, et al., *Langmuir*, **26** 8201-8206 (2010), 'Crystalline Structures of Alkylamide Monolayers Adsorbed on the Surface of Graphite'.

Bhinde, et al, proceedings of the ECIS 2009, Antalya, Turkey, *Progress in Colloid and Polymer Science*, **137** 5-8 (2010), 'The structure of dodecanamide monolayer adsorbed on graphite'.

Aldehydes on graphite:

Phillips, et al, *Thin Solid Films*, **519** 3123-3127(2011), 'Adsorption of Odd Aldehydes on a graphite substrate'. DOI:10.1016/j.tsf.2010.12.084.

Phillips, et al, *J. Physical Chemistry,* **C*114*** 6027–6034 (2010), 'Adsorption of aldehydes on a graphite substrate: Combined thermodynamic study of C6-C13 homologues with a structural and dynamical study of dodecanal'. DOI:10.1021/jp911069t.

Halogen bonding systems on graphite:

Clarke, et al, *Chem. Comm*. **47,** 2526 – 2528**,** (2011). 'Observation of a two-dimensional halogen-bonded cocrystal at sub-monolayer coverage using synchrotron X-ray diffraction' **DOI:** 10.1039/C0CC04400H.

Brewer, et al, *Langmuir,* **29**, 14903-14911 (2013). 'Combined diffraction and DFT calculations of halogen bonded co-crystal monolayers', http://dx.doi.org/10.1021/la402910a

Clarke. et al., *Mol Phys.,* **109** 477-481 (2010), 'Monolayer Structure of 4,4' bipyridine on Graphite at Sub-monolayer Coverage'.

Alkanes on MgO:

Arnold, et al, *Physical Review* **B74** 085421(2006). 'Structure of an n-butane monolayer adsorbed on Magnesium Oxide (100)'.

Alkanes on BN:

T. Arnold et al, Structure of Normal-Alkanes Adsorbed on Hexagonal-Boron Nitride

J. Phys. Chem. C, (2014) **118**, pp 2418–2428, DOI: 10.1021/jp4063059

Review

Arnold T. and Clarke. S. M., *Current Opinion in Colloid and Interface Science*, **6** 118-125 (2011), 'Diffraction from Physisorbed Layers'. DOI:10.1016/j.cocis.2011.11.003.

2) *Truncation rod experiments:*

Surface crystallography: very high resolution studies.

On Calcite.

Erika Callagon, et al, Incorporation of Pb at the Calcite (104)−Water Interface, dx.doi.org/10.1021/es5014888 | Environ. Sci. Technol. (2014) **48**, 9263−9269

S. Hofmann, et al, Visualising the molecular alteration of the calcite (104) – water interface by sodium nitrate *Scientific Reports* **6**, Article number: 21576 (2016) doi:10.1038/srep21576

On Mica.

S. Pintea, et al. DOI: 10.1021/acs.langmuir.6b02121 *Langmuir* (2016) **32**, 12955−12965, Solid−Liquid Interface Structure of Muscovite Mica in CsCl and RbBr Solutions.

3) *Neutron and Xray reflection (structure normal to surface)*

Very extensive body of data of molecular and polymeric systems adsorbed from water and oil onto a wide variety of substrates, SiO2, Alumina, mica, metals, metal oxides, minerals, graphene. Etc. Originally used for studies of the liquid/air surface. Lots of work on solid/liquid and some recent liquid/liquid interface studies [A. Zarbakhsh, et al, Neutron Reflection from the Liquid−Liquid Interface: Adsorption of Hexadecylphosphorylcholine to the Hexadecane− Aqueous Solution Interface, *Langmuir*, (2005), **21**, pp 11704–11709, **DOI:** 10.1021/la0518086].). Non-invasive.

Gives the absolute composition and layer thicknesses of the adsorbed surface layers - in situ. Isotopic contrast to study multicomponent mixtures. Requires large very flat surfaces (ideally several square centimetres) and a neutron source. Recent work includes studies under external fields.

Silica

G. Fragneto et al, *Langmuir*, (1996) **12**, pp 6036–6043, DOI: 10.1021/la9604644, Neutron Reflection from Hexadecyltrimethylammonium Bromide Adsorbed on Smooth and Rough Silicon Surfaces.

Wang, X., et al, *Langmuir*. **29**, 5520−5527 (2013). 'Cation-Bridging Studied by Specular Neutron Reflection'. dx.doi.org/10.1021/la400767u.

Minerals:

Calcite:

Stocker, et al *, Progress in Colloid and Polymer Science,* **139,** 91-99 *(*2012). Neutron reflection at the Calcite-Liquid Interface', DOI: 10.1007/978-3-642-28974-3_16.

Stocker, et al., *J. Coll. Inter. Sci.,* **418C** 140-146 (2014). 'Adsorption of Aerosol-OT at the Calcite/Water Interface – Comparison of the sodium and calcium salts'. DOI: 10.1016/j.jcis.2013.11.046.

Mica:

Miller, K. L., et al *J. Appl. Cryst.* **47**, 1638-1646 (2014), 'Specular Neutron Reflection at the Mica Water Interface – Irreversible Adsorption of a Cationic Dichain Surfactant'. DOI:10.1107/S1600576714016318 .

L.. R. Griffin, et al. 'Direct measurements of ionic liquid layering at a single mica-liquid interface and in nano-films between two mica-liquid interfaces'. Physical Chemistry Chemical Physics, (2017), **19**, 297 – 304.

Metals/oxides

Iron oxide

Wood, M. H., et al, *Langmuir*, **29** 13735–13742 (2013), 'Hexadecylamine Adsorption at the Iron Oxide-Oil Interface', DOI: 10.1021/la4018147.

Campana, M., et al, *Langmuir*, **27** 6085-6090 (2011), 'Surfactant Lubricant at the Metal-Oil Interface'. DOI: 10.1021/la200670w.

Steel

Wood, M. H., et al, *J. Phys. Chem*, 120, 5405-5416 (2016). 'Using Neutron Reflectometry to Discern the Structure of Fibrinogen Adsorption at the Stainless Steel/Aqueous Interface'. DOI: 10.1021/acs.jpcb.6b02341.

Nickel

Wood, M. H., et al, *Langmuir* 31 7062-7072 (2015). 'Polarized Neutron Reflectometry of Nickel Corrosion Inhibitors'. DOI: 10.1021/acs.langmuir.5b01718.

Alumina

Hellsing, M. S.;et al, Effect of Concentration and Addition of Ions on the Adsorption of Aerosol-OT to Sapphire. Langmuir 2010, 26, 14567−14573.

Lee, S. Y., et al., *J. Coll. Interface Sci.,* 407 348-353 (2013), 'Adsorption of Sodium Hexanoate on α-Alumina'. DOI: 10.1016/j.jcis.2013.06.019,

R. J. L. Welbourn, et al, DOI: 10.1021/la504837s Langmuir 2015, 31, 3377−3384, Neutron Reflection Study of the Adsorption of the Phosphate Surfactant NaDEHP onto Alumina from Water.

Copper

R. J. L. Welbourn et al, *Corrosion and Inhibition of Copper (II) Oxide in Hydrocarbon Solution on a Molecular Level Investigated using Neutron Reflectometry and XPS*, 2017, 115, 68-77 *Corrosion Science* DOI: http://dx.doi.org/10.1016/j.corsci.2016.11.010.

Others

Polymer surfaces

Turner, S. F., et al., *Langmuir* 21 10082-10088 (2005). 'Adsorption of gelatin to a polystyrene/water interface as a function of concentration, pH, and ionic strength'.

3) Adsorption to the surface of particles/colloids from liquids

Small angle xray (SAXS) and neutron scattering (SANS): Introduction to the method:

e.g. http://www.isis.stfc.ac.uk/learning/neutron-training-course/downloads/soft-matter/introduction-to-sans-201414792.pdf

Used to quantify composition and layer structure of molecules on small particles in suspension. SANS can again exploit the contrast variation approach to probe each component of mixtures.

Spectroscopic methods

1) Sum frequency generation (SFG) – surface specific

   Using the break in centrosymmetric symmetry at a surface to characterise the surface IR spectroscopy of adsorbed species. Ideal for determination of adsorbed chemistry (eg CO_2H vs CO2 -), absolute orientation of molecular dipoles, adsorbate molecular orientation and details of conformational order of alkyl chains. Can get in-plane spatial distribution on micron lengthscales with an SFG microscope. Can probe adsorption in-situ under static and applied fields such as shear, temperature etc. ideally on a flat, reflective surface. Metallic substrates can have some enhancement, relative to dielectrics. E.g.

   Wood, M. H et al, *Langmuir*, *29* 13735–13742 (2013), 'Hexadecylamine Adsorption at the Iron Oxide-Oil Interface', DOI: 10.1021/la4018147.

   Wood, M. H., et al., *Langmuir*, 32, 534–540 (2016). 'Comparative Adsorption of Saturated and Unsaturated Fatty Acids at the Iron Oxide/Oil Interface.',DOI: 10.1021/acs.langmuir.5b04435.

2) Related spectroscopy – surface sensitive

   RAIRS/ ATR are reasonably standard methods that enhance the contribution of IR bands from a surface species, relative to bulk contributions.

   Recent method advances such as PM IRRAS (which exploits polarisation to enhance the contribution from a surface) can be helpful.

3) AFM-IR – In outline one might consider that thermal expansion of an adsorbed layer by uptake of IR radiation is detected by an AFM tip. Hence very high in-plane spatial resolution (approx. 10nm). Used for chemical group identification on spatially heterogeneous surfaces. Presently only used for 'dry' systems (not under liquids).

Thermodynamics/Calorimetric methods

1) Differential Scanning Calorimetry

Thermal transitions arising from a monolayer adsorbed from a liquid on a powdered substrate can be identified and followed with changing conditions/composition.

For example, the melting point of a monolayer adsorbed on a substrate can be identified ('pre-solidification'). The variation of this monolayer melting point with composition reveals: preferential adsorption from mixtures, non-ideality of mixing in the 2D layer, identification of 2D phase diagram including: ideal mixing, phase separation, non-ideal mixing, peritectics, dystetics (2D stoichiometric complexes)..etc. etc.

Example Systems:

Alkanes on Graphite

P. Espeau and J. W. White, Thermodynamic properties of n-alkanes in porous graphite, J. Chem. Soc., Faraday T rans., (1997), **93**, 3197È3200

Castro, M., et al, *Journal of Physical Chemistry*, **B102** 10528-10534 (1998). 'Competitive Adsorption of Simple Linear Alkane Mixtures onto Graphite'.

Clarke, S.M.,et al, *Chemical Physics Letters*, **373** 480-485(2003), 'A quantitative parameter for predicting mixing behaviour in adsorbed layers: the 2D isomorphism coefficient'

Castro, M et al *Physical Chemistry Chemical Physics,* **1**, 5017-5023 (1999). 'The Investigation of Mixed Monolayers Adsorbed from Solution: Octane and Nonane Mixtures on Graphite'.

Alcohols

Messe. L.et al., *Langmuir*, **18** 4010-4013 (2002). 'The mixing behaviour at the solid/liquid interface: binary monolayers of linear alcohols adsorbed on Graphite'.

Messe, L et al, *Langmuir* **18** 9429-9433 (2002). 'Mixing Behaviour at the Solid/Liquid Interface: Binary Alcohol Monolayers on Graphite'.

Alkanes and alcohols mixtures on graphite

Messe, L.,et al, *Langmuir,* **21** 5085-5093 (2005), 'Alkane - Alcohol Mixed Monolayers at the Solid/liquid Mixture Interface'.

Carboxylic acids on graphite

Bickerstaffe, A. K., et al, *Physical Chemistry Chemical Physics*, **6** 3545-3550 (2004), 'Mixing behaviour of Carboxylic acids adsorbed on Graphite'.

Amines on graphite

Cheah, N. P., et al, *J. Phys. Chem.* **B108** 4466-4469 (2004), 'The Formation of Solid Monolayers of Linear Amines Adsorbed on Graphite from the Liquid'

Others

Duim, W. C. and Clarke. S. M., *Journal of Physical Chemistry*, **B110** 23853-23859 (2006), 'Adsorption and Mixing Behaviour of Ethers and Alkanes at the Solid/Liquid Interface'.

Sun, C., et al, *Langmuir*. **27**, 3626-3637 (2011), 'Bulk and Adsorbed Monolayer Phase Behaviour of Binary Mixtures of Undecanoic Acid and Undecylamine: Catanionic Monolayers'. DOI: 10.1021/la1048198.

Phillips, T. K et al *J. Physical Chemistry,* ***C*****114** 6027–6034 (2010), 'Adsorption of aldehydes on a graphite substrate: Combined thermodynamic study of C6-C13 homologues with a structural and dynamical study of dodecanal'. DOI:10.1021/jp911069t.

Can be used to observe layer by layer freezing at a surface and other transitions.

Messe. L., et al, *Journal of Colloid and Interface Science*. **266** 19-27 (2003). 'Layer by Layer surface freezing of linear alcohols at the Graphite/Liquid interface'.

2) Solution depletion adsorption isotherms.

Gives the amount adsorbed as a function of solution concentration. Can infer molecular orientation/structure. With suitable analytical tools can probe competitative adsorption, non-ideal behaviour etc.. Temperature dependence can be used to give ΔH and ΔS of adsorption. Cheap and relatively easy (with appropriate care).

3) Titration/Ph

Means of characterising surface groups in water/non-aqueous systems by their pKa and amount. Extensive literature from water/environmental Chemistry (e.g. Book: Aquatic chemistry, Stumm and Morgan) with equilibrium constants, binding mechanisms of organics on substrates etc..

Used to identify potential determining ions and indifferent electrolytes, etc.

Dynamic methods

1) NMR low field

T1/T2 as an indicator of what's adsorbed and binding enthalpy from relaxation. Lots of interest from catalysis characterisation porous solids etc.. (e.g. Lynn Gladden et al, Cambridge).

e.g. C. D'Agostino, et al, "Effect of paramagnetic species on T_1, T_2 and T_1/T_2 NMR relaxation times of liquids in porous $CuSO_4/Al_2O_3$", *RSC Advances*, 2017 .

2) High field NMR and 'dynamic contrast'

Uses the idea that adsorbed molecules are 'static' and molecules in solution are mobile. This mobility difference can be detected by NMR. Isotopic labelling is used to identify preferential adsorption of mixtures. E.g.

Alba, M.D., et al. *Solid State Nuclear Magnetic Resonance,* 23 174-181(2003), 'NMR Study of n-dodecane adsorbed on Graphite'.

Alba, M. D., et al, *Journal of Physical Chemistry*, *113* 3176-3180 (2009). 'Preferential adsorption from binary mixtures on graphite: the Decane–Heptanol System'.

Alba, M. D., et al, *European Physical Journal-Special Topics,* 167 151-156 (2009). 'Phase separation of carboxylic acids on graphite surface at submonolayer regime'.

Alba, M., et al , *Solid State Nucl. Mag. Resonance*. 40 138-143 (2011), 'Application of the Solid State NMR to the study of the alcohol/alkane mixtures adsorption onto graphite'.

Cross polarisation NMR measurements have been used to give the binding and spatial distribution of metal ions on clays (relevant to heavy metal ion capture).

M. D. Alba , et al Physics and Chemistry of Minerals, (2004), **31**, pp 195–202
Structural localization of Al^{3+} ions in aluminosilicates: application of heteronuclear chemical shift correlation to 2:1 phyllosilicates

3) Incoherent neutron scattering (IQNS)

As for dynamic contrast NMR, uses the difference in adsorbed species mobility relative to the bulk liquid to characterise what's absorbed and give preferential adsorption. Exploits contrast variation isotopic labelling to identify the behaviour of mixtures hence can be used to probe combinations of very similar species (e.g. octane and decane)

In favourable cases can be used to characterise the nature of motions of adsorbed species (eg translational vs rotational motion from the Q dependence).

Castro, M et al, *Journal of Physical Chemistry*, **B101** 8878-8882 (1998). 'Solid Monolayers Adsorbed at the Solid-Liquid Interface Studied by Incoherent Elastic Neutron Scattering'.

Castro, M., et al *Journal of Physical Chemistry*, **B102** 10528-10534 (1998). 'Competitive Adsorption of Simple Linear Alkane Mixtures onto Graphite'.

Castro, M. et al,, *Journal of Physical Chemistry,* **B105** 8577-8582 (2001). 'Preferential Adsorption of Binary Mixtures of Short n-alkanes: the Octane-Decane System'.

Castro, M. et al, *Physical Chemistry Chemical Physics,* **3** 3774-3777 (2001). 'Adsorption Behaviour of the Binary Mixtures of Octane and Nonane at Sub-monolayer Coverages on Graphite'.

Parker, J et al, *Surface Science* **601** 4149-4153 (2007). 'Preferential adsorption of fluorocarbons and hydrocarbons adsorbed on graphite'

Parker, J. E.and Clarke. S. M., *Colloids and Surfaces A, Physiochemical and Engineering Aspects*, **298** 145-147 (2007). 'Solid Monolayers of fluorocarbons Adsorbed on Graphite from Liquids'.

Arnold, T., and Clarke. S. M., Langmuir, **24** 3325-3335 (2008). 'Thermodynamic investigation of the adsorption of amides on graphite from their liquids and binary mixtures'.

Wang, G., et al *Langmuir*, **24** 2501-2508 (2008), 'The Behaviour of Binary Alcohol Mixtures Adsorbed on Graphite using Calorimetry and STM'

Castro, M, et al *Physical Chemistry Chemical Physics,* **1**, 5203-5207 (1999), 'Anomalous Behaviour of Pentane Adsorbed at the Graphite/Liquid Interface'.

Can be used to observe layer by layer freezing at a surface

Messe. L., et al, *Journal of Colloid and Interface Science*. **266** 19-27 (2003). 'Layer by Layer surface freezing of linear alcohols at the Graphite/Liquid interface'.

K. W. Herwig, et al, J. Chem. Phys. 107 (13), (1997), Quasielastic neutron scattering and molecular dynamics simulation studies of the melting transition in butane and hexane monolayers

adsorbed on graphite ..'The elastic scattering observed above Tm is consistent with the coexistence of solid monolayer clusters with a fluid phase, as predicted by the simulations. For T/Tm>1.3, the elastic scattering vanishes from the neutron spectra where the simulation indicates the presence of a fluid phase alone. '..

Others

1) **Surface Force Balance/Microscopy** - Molecular level adsorption on mica by ions and molecules. Introduction: Intermolecular and Surface Forces (Third Edition), *Jacob N. Israelachvili,* ISBN: 978-0-12-375182-9.
   Recent example:
   Smith A.M. et al Switching the Structural Force in Ionic Liquid-Solvent Mixtures by Varying Composition, Phys. Rev. Lett. 118, 096002, 2017