Structure, Symmetry, Matter, Chemistry.

-Soumyajit Roy

1.1. Why Chemistry?

As you open this file, as I write these words on my Carbon X1 Think Pad, even as I process these thoughts essentially, I am meandering in a maze of matter. Or is it better to say that matter meanders in a matrix. Chemistry is the code that wraps and warps this matrix. Sadly, enough we are blissfully ignorant of chemistry and "stuff that matters"! From the birth of the Universe to the birthing of this note, everything is chemistry. The former is cosmic cooking the latter is a spatio-temporal dancing of matter that can be written and backspaced out to oblivion. (I mean typing out or erasing it away on my Think Pad!) So, from the birth of the Universe to the experience of her finest creations humans, it's all chemistry that matters! From the making of our clothes to the finest wining and dining to drugs defining modern human existence, modern world is woven around chemistry. But what was the first time we experienced chemistry? I guess rather sadly, the answer is a resoundingly wrongly etched in our memory as the smelly lab of our schools when we were first thrusted with a gigantic table that we were forced to cram without understanding, obnoxious odor and formulas and arcane symbols. But, is that so?

The wafting smell of rose (phenyl ethyl amine). The freshly brewed coffee (caffeine). The lovely bouquet of wine (polyphenols). The inexplicable feeling of fluttering warmth at the sight of that special one (oxytocin). The touch of that lively liquid that sustains life (water). These are the essence of chemistry in action. Chemistry is the very silent symphony of almost everything experiential we see, smell, taste, touch and hear everyday around us. Chemistry is an artwork that has been developed and gifted to us so that we may start with the knowledge what Nature has cooked and curated in crucibles of her lab and gifted us with care curated for more than 14 billion years! In the words of one of our pioneering leaders of chemistry, Jean-Maire Lehn, we start our evergreen exploration compressed and coded in nine alphabets: CHEMISTRY!
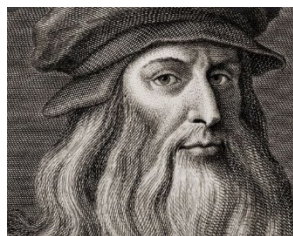
THE ESSENCE OF CHEMICAL SCIENCE THUS FINDS ITS FULL EXPRESSION IN THE WORDS OF LEONARDO DA VINCI: "WHERE NATURE FINISHES PRODUCING ITS OWN SPECIES, MAN BEGINS, USING NATURAL THINGS AND IN HARMONY WITH THIS VERY NATURE, TO CREATE AN INFINITY OF SPECIES."

- JEAN-MARIE LEHN -
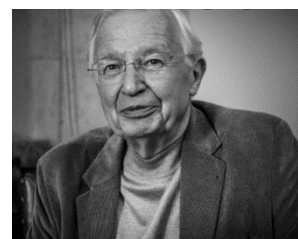
DISCLAIMER: Sections marked in Blue in this document are ONLY for the curious few. One can safely skip those parts!

1.2. How Chemistry touches you? Your first experience with Chemistry. Chemistry is Life!

I guess some of us think it's the smelly chemical lab. Some think it is those horrific encrypted equations that we learn in school. In fact, our first experience of chemistry is the air we breathe in. Oxygen. Next one is perhaps as we play with water and ice, and have warm shower. Finally, the food we eat and digest and derive our energy from, as the chemical energy stored in food is released as it is burnt with the oxygen, we breathe in. In fact, the green plants we see around us, is also chemistry. They store sunlight (energy) as they split water (H_2O). That energy is converted into chemical energy as they fix carbo (CO_2) with hydrate (H_2O) and dish us carbohydrate, so that we can break it as we breathe with Oxygen (O_2). So, in a way the central design of life process centers around 2 very simple chemical relations: one that of photosynthesis and other that respiration. Also note water strikes the sweet balance. Water is a liquid, and electron, proton, oxygen reservoir and rightly the crucible of life. So, we will start our journey with water and its structure as a liquid. But first a brief glance at the **equation of life** below:

Equation of Life

Photosynthesis:

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

Respiration:
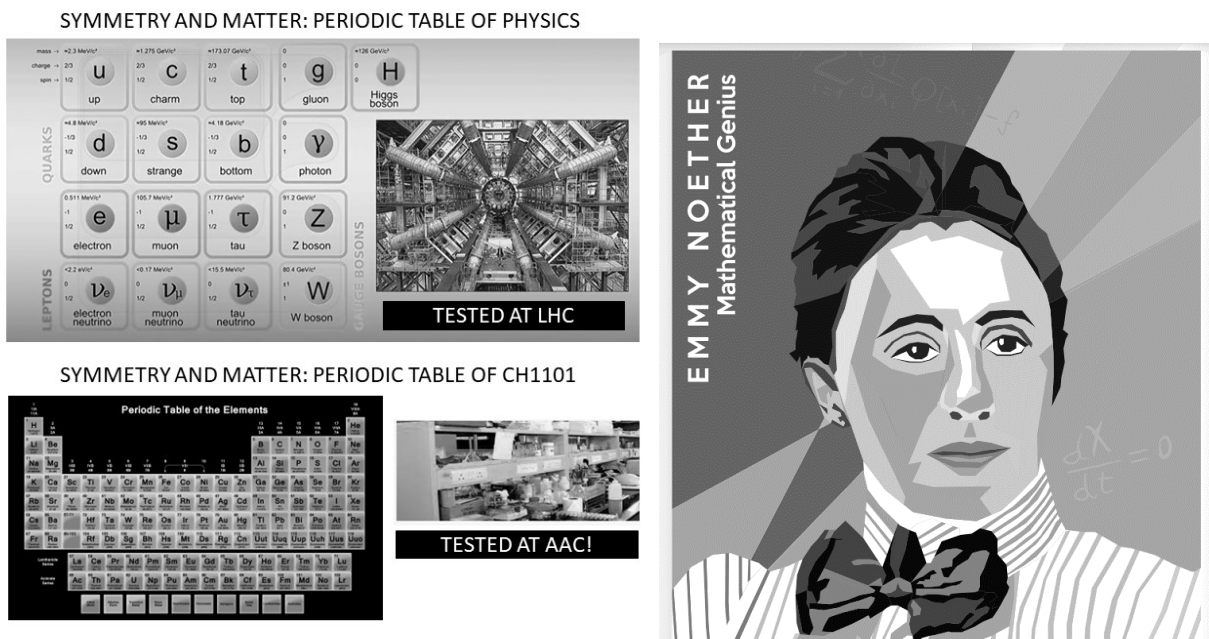
$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

1.3. On Origin of Matter:

We now move from equation of life to origin of matter and its structure thereof that makes life. Chemistry in fact deals with matter. Semantically the word matter is rooted in the Sanskrit word 'Matra'. In fact, 'Matra' is perceived as the limit or dimensionality in its original sense. So, it is to be noted that the early perception of Indian Seers and Material Scientists as the limit of existence was profound to say the least. Is origin of matter understood? In fact, we have a framework rooted in Mathematics and Physics (QCD). It can also be perceived from the angle of simple symmetry. We will invoke the last route as it embraces all the approaches and provides scope to accommodate any emergent view (perhaps from Chemical Science) in the future to be woven into it. Initially if one reasonably hypothesizes that there was absolute singularity (high symmetry). Then there was perturbation and loss of symmetry. Such a loss in symmetry is correspondingly compensated by a 'current of action' that led to origin of matter and energy which in turn are interconvertible. Such an ideation is attributed to Emmy Noether's first theorem. We state it here:

"If a system has a continuous symmetry property, then there are corresponding quantities whose values are conserved in time."

As of now, we leave the question of origin of mass here and we note that the above view automatically embraces the Higg's Field and related frameworks consistently in the matter of origin of mass. It's our view that Noether's theorem will also be sufficient to embrace and accommodate any theory of origin of

matter (even emergent) as it deals with symmetry rules leading to the origin of conservation of variables be it energy, momentum and of course mass is also thus included. We give a simple depiction of the 2 fundamental symmetric tables that describe everything we see around us, one is that of the Physicists and the other is that of the Chemists. Please look up more on Noether's Theorem depicted at the website of the Perimeter Institute. (https://insidetheperimeter.ca/noethers-theorem-kindergarten-phd/)

SYMMETRY AND MATTER: PERIODIC TABLE OF PHYSICS

TESTED AT LHC

SYMMETRY AND MATTER: PERIODIC TABLE OF CH1101



TESTED AT AAC!

EMMY NOETHER
Mathematical Genius

1.4. Periodicity, Parsimony and Symmetry: Some Basic Notions

Going a step afar from Emmy Noether's idea, we look at the meaning of symmetry in a simpler way. Herman Weyl, another Mathematician, elucidated the idea of symmetry from three perspectives. Of which the two elementary perspectives he proposed are: 1. Symmetry from the perspective of the object; 2. Symmetry from the perspective of operations.

1. Symmetry from the perspective of Object: Consider a circle. Whatever angle you rotate it in plane with the rotational axis going perpendicular to the plane of paper and passing the center of the circle, the circle remains the same. It is thus a symmetric object.
2. Symmetry from the perspective of Operation: Consider the same circle. Now if you rotate it by any angle, which is a symmetry operation, it remains the same. So, the circle is symmetric w.r.t such operations. Such simple symmetry operations have nice names like C_n, C_1, C_2, C_3, etc.

On an even simpler level, we now look at the meaning of symmetry. We ask the question can we depict the symmetry of the circle more tangibly? To do so let us consider the motion of a particle along the circular axis and let us depict the trajectory of its motion and see what we observe. In fact, we observe a wavy simple harmonic motion. (See the Figure below.) In other words, a periodic motion like that of a simple harmonic motion is a projection of circular motion. Thus, from the present line of reasoning you can at least conceptually connect that at a more elementary level, periodicity is Nature's way of repeating her repertoire. Periodicity, a result of symmetry, is in itself circular, repetitive.

Simple Harmonic Motion (Periodic Motion) is a Projection of Circular Motion
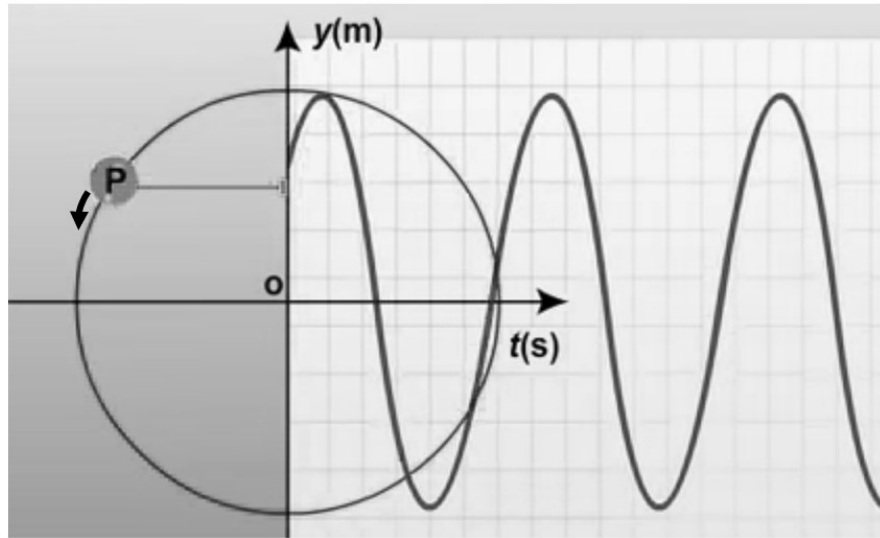
It is in fact intrinsic in Nature's design such that She does not need to spend too much on diversity at the more elementary level (can be thought of as Parsimony). Now, let us zoom out and we will appreciate Noether's genius more. At the heart of even actions that involve motion even there one observes Nature's thrifty approach and conservation principles emerge. Such conservations as noted and rooted in Noether's theorem are not only manifest in the conservation laws of Nature but also lies at the very heart of causal connections or causality. (Cause leads to effect and reverse). Needless to say, by now, it is obvious perhaps to us all, that the science of Matter, has to have a periodic pattern at her core. In fact, that is the periodic table, discovered by Dmitry Mendeleev, one of the finest works of classifications by Mankind till date, which in turn tells us how chemical science and chemistry of matter makes sense!

1.5. Tiling, Packing, Solids and Curvature: Some Elementary Ideas

Have you ever noticed that when you are in a rush and have to leave on a Friday afternoon back home with all your worn clothes, you are not able to squeeze them in your bag, when not folded or packed properly? It has got to do with how you are packing. Monday, when you came to college, your clothes were most likely packed by your mom, very properly, so there was space even for some of her home made delicacies. But now, it is Friday and you still cannot pack it in! Well, like every mom, Mother Nature likes packing. When we are talking of 3D-space we are talking of packing and when we are talking of tiling. Let us then start with tiling.

When we look at a 2D-plane, essentially Euclidean plane, the simplest tiling that one can think of is that of is a honey-comb (See Figure). It is essentially a set of hexagons placed next to each other so that the entire surface is covered. In fact, a hexagon, or for that matter any polygon, can be broken (decomposed) into a triangle. Hence, in principle any 2D surface can be triangulated (covered with triangles). So, the moment a surface is triangulated, one is able to 'compress' information. Nature by this simple operational logic of symmetry behaves thrifty! We as humans try to appreciate this logic in forms of mathematical operators like that of C_1, C_2, etc. as symmetry operations. Instead of putting so many hexagons/triangles together one can write their numbers around a common vertex, orientation and the pattern in which they are disposed. In this way an entire array of polygons in a plane can be represented very simply as a code

containing the above 3 information! Note: this is only possible because symmetry in a subtle way helps us in reducing the information, which in turn can be encrypted in the language of Mathematics. Indeed, thus packing is a way of Nature to preserve parsimony.

Now that we have looked at hexagonal tiling, and its triangulation thereof let us now consider a slightly more complex scenario. We replace one of the hexagons with a pentagon. Oops! Now it so happens that the plane 'curls' up! It is no more confined to 2D but becomes 3D. To connect it with a real-life example, now that the Football world cup is going on and if we look at any football (not necessarily only at Messi!), we will see that there are 12 pentagonal blocks and 20 hexagonal blocks. It is fixed and it comes from a critical symmetry restricting requirement for construction of 3D closed surfaces.

We will now look at possibilities to close 3D space using 2D blocks as was envisaged by Greek Philosopher Plato. Following his honorable observation such solids which are made of one type of vertex (meaning only one type of polygon, like triangle, square, pentagon) they are known as Platonic solids. Now such Platonic solids are only five: Tetrahedron (only with 4 triangular faces: Tetra = > 4, Hedron => Face), Cube (with 6 squares), Octahedron (with Octa = > 8 triangular faces), Icosahedron (with Icosa =>12 triangular faces) and Dodecahedron (with Dodeca => 20 pentagonal faces). Historically, the Greeks used them to represent basic elements of Nature: Fire, Air, Water, Earth and Sky! So, these were 'the sacred solids of the Greeks' and they are highly symmetric. In fact, it is also worth noting that Johannes Kepler in his magnum opus *Harmonice Mundi* construed the first model of the celestial universe with these solids encased inside each other, and showed that the distance of the first five planets followed such encapsulation from his calculations of planetary distances in our solar system. He believed that these sacred solids contained spheres and they held the keys to the "music of the spheres"! Now we take a closer look at these solids to appreciate the operation of symmetry elements a bit closer.

A triangle essentially is invariant by a rotation of $360^o/3$ and thus it is denoted by C_3. Likewise, now you can easily guess the symmetry elements of a square will be C_4, pentagon C_5 and hexagon C_6 very easily. (Can you tell how will you represent the symmetry element of a cylinder?) Let's anyway enjoy this music of symmetry a bit closer!

Now a 2D plane is considered as Euler plane. The geometry of 2D is known after the Greek Mathematician Euler as he was the master who among many other pioneering works conceptualized the framework of 2D geometry. So, no wonder, Euler would contemplate more on how would his geometry of 2D would embrace their divergence from 2D to 3D! In fact, it was the great Mathematician Archimedes, who took up this task and started carving out solids by literally cutting their corners, or even fusing two Platonic solids into each other! Yes, you guessed it correctly! He came to the geometric description of Football in this process and came up with solids which were polyhedron with two types of vertices! We will now kick around our Football armed with boots of symmetry and with skills of Profs. Archimedes and Euler.

The Archimedean Dribble: Archimedes proposed that to create a Football we set off with an Icosahedron and cut its $12C_5$ vertices to make $12C_5$ (pentagonal) faces and if we do it very carefully in this process, we will create $20C_6$ faces. With such a golden pass, it was a simple cakewalk for Prof. Euler to score a goal!

The Euler's Relation: From the above line of reasoning Prof. Euler came to his famous relation to describe any closed surface geometry enclosed by Archimedean solid. The relation is:

$E = F + V - 2$

where, E => Number of Edges (in case of our Football these edges are lines with C_2 symmetry)

F => Number of faces (in case of our Football these are 20 hexagonal faces with C_6 symmetry)

V=> Number of vertices (in case of our Football these are 12 pentagonal faces with C_5 symmetry)

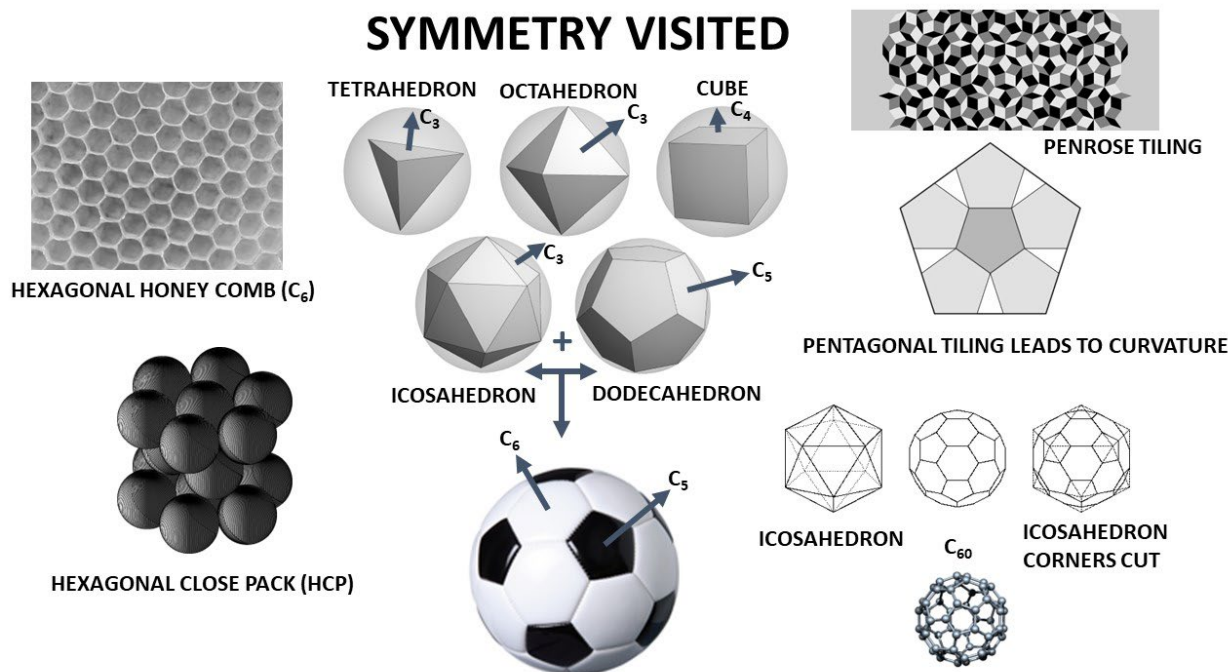Hence following Prof. Euler we immediately arrive that our Football has $30C_2$ edges!

"Isn't it beautiful Darling!" A very British accent touches us and we are reminded of another British augmentation with such Football symmetry and we find ourselves meeting Profs. Harry Kroto, Dick Smalley (US national though!) with their discovery of a new allotropic form of Carbon: Fullerene, fondly known as Bucky Ball! It's C_{60}. So now that we know the elements of symmetry of C_{60} are $12C_5$, $30C_2$ and $20C_6$ can you quickly deduce how the formula is C_{60}? We now see the real power of symmetry!

But this story cannot be complete without considering the genesis of the name Fullerene. We owe it to an American Architect, Philosopher, Inventor, Buckminister Fuller, who came up with the structure of earth as a Football and raised architecture of a Football known as Geodesic structures! It was to honor this architectural intellect Profs. Kroto, Curl and Smalley (Nobel Laureates of Chemistry of 1996) named this form of Carbon as Fullerene.

We still stay on a bit more with our English friends. Enters today's genius Prof. Roger Penrose (Nobel Laureate of Physics of 2020) and he comes up with the only exceptional 5-fold tiling (Penrose tiling) to cover a 2D- space without letting it curl up.

So if we are now allowed to linger a little longer thinking with our symmetry hat, we can understand that if we are to have a regular array of points (let's call them lattice points) to tile an array first in 2D (or a 2D-lattice) and later translate it in one more dimension to have a 3D lattice, with our present understanding we can appreciate that we cannot have a surface tiled if we have C_5 symmetries! In fact, this sentence held ground until Dan Shechtman, an Israeli structural chemist, "discovered a type of crystal so strange and unusual that it upset the prevailing" concept of crystalline existence! He came up with Quasi-crystals which had C_5 symmetries in them! Dan Schechtman was awarded the Nobel prize in 2011 in Chemistry for this discovery.

So starting from a startling insight from Emmy Noether on the symmetry of actions, to Hermann Weyl's basic notion of symmetry we have seen symmetry applied in Football, and have seen at least few breakthrough discoveries with unique states of matter (crystal, liquid crystal) and a new elemental form Fullerene altogether been discovered and designed. We will continue to traverse this forest of structural matter and map our own working compass of chemistry aided with symmetry! I hope you are still with me in this structural excursion!

SYMMETRY VISITED

HEXAGONAL HONEY COMB (C_6)

HEXAGONAL CLOSE PACK (HCP)

TETRAHEDRON — C_3

OCTAHEDRON — C_3

CUBE — C_4

ICOSAHEDRON — C_3

DODECAHEDRON — C_5

C_6 / C_5

PENROSE TILING

PENTAGONAL TILING LEADS TO CURVATURE

ICOSAHEDRON

C_{60}

ICOSAHEDRON CORNERS CUT

1.6. Structure: What Is It? Some Elementary Considerations

What is structure? Wait, a minute. Just take your eyes off from this book and look around. What do you see? If you are in a bookstore, you see shelves of books, categorized, organized, *structured.* If you are in your study and if you happen to be like me, if you look around, you see books, notepads, pens, pencils, scattered around and it is messy, not organized and *not structured.* Well, wait a minute. Is that so? Does something lacking that apparent order mean lacking a structure? It does not. Here in the next few pages and chapters we will explore the idea of structure. We will branch out, zoom out and then zoom in to have a simplistic view of the world around us through structure. We will be provocative and propose that a systematic study to understand structure in itself and come up with a formalism to look at structure which is at rest (static) and which is ever evanescent (dynamic) and this approach can be a way forward to navigate through a world of matter and chemistry that usually evades our vision. Still interested? Let's get started!

We arch back to the beginning and ask again: What is structure anyway? Very simply it is in fact how things (points) are in relation to one another (in spatial-temporal domain). This relation can be with respect to position, properties, parameters, you name it. In this note, in keeping with our ongoing line of thoughts following symmetry and its lack thereof, we will take a simple logical approach steeped in symmetry or its absence thereof as we take baby steps toward the concept and idea of structure.

We start from the thing you are holding in your hand. For the sake of convenience let us consider that it is a book. What is the structure of this book? It has a shape. It has a fixed form, occupying space, (and does not change its shape over time): it is a solid. A bit more detailed investigation of it will reveal that it is a collection of pages which are bound in a certain way. This certain way, the relation, imposes restrictions on its properties, for example how you can open it. How you can keep it open. Take a bunch of same number of pages, with same size and shape and stitch them and they take the shape exactly the

way in how they are in the book you hold. What does it tell us? The relation among its constituent pages imposes a restriction as of how it should look like.

Structure is a reflection of restrictions imposed by its relations. Such relations in fact are symmetry restrictions which we saw earlier. What else? It takes up space. Now here is another funny twist to its occupancy of space. Tear it up and spread it by tiling the pages on a wall, though it will take up now more area, yet the volume of space it occupies remains exactly the same and so does its weight or loosely speaking its mass.

Now imagine if you keep on reading this book time and again and keep opening and closing it, ear-marking it and after significant times of such repetition the book will 'deform', it will lose its shape, its physical structure will alter a bit. This is so because in course of such usage essentially you are pumping in more and more energy with time which is turn in inducing deformation in its structure and altering it. Can you somehow relate it with Noether's theorem we talked of earlier here?

So, structure essentially is a manifestation of energy, in relation to various points in space and time with the constituents (say spheres or atoms or electrons) as we will see later in more details. We dwell a bit more upon this rather common aspect of structural change induced by energy with time taking cues from this book.

Imagine your young toddler cousin got hold of this book and crumpled some pages within! When she did that, there was sound, and now you are unable to fold it and close it back to its original form. Essentially what has happened to your book in your toddler's hand is as following. When she was crumpling the pages the binding energy of the pages of the book got a bit transformed into sound energy (the symmetry was lost and the price paid by energy) and that led to changes in the structure (lowering the local symmetry of the book) of the pages of the book, leading to it deformation. Result? Now you cannot close the book properly.

If you think a bit more, the toddler in fact applied this extra energy temporally (or with time) through the structure of her hands to set forth this deformation in the first place, which stays over time. Hence, structure and energy has interacted in this particular case over both space and time. This is an example where this *dynamic* deformation (read *structure*) has led to a new structure which contains this deformation in its *static structure*, that stays over time.

Thus, if the nature of all the associated interactions of your toddler cousin is modeled or rather if it can be modeled then the evolution in *dynamic* structure leading to a new *static structure* can be predicted. In the present case, the prediction of the toddler's behavior is difficult hence the prediction as of when the book will suffer its fate of deformation is difficult as well!

Imagine that the book has in store a bit more of adventure in store in the hands of our toddler. You were drinking a glass of water and this glass was left near the book. She kicks the glass and the pages get wet by the water spilled on it. You wipe the water off, try your best to dry it, still the pages *swell* up and looks deformed! What has happened?

The water has its own structure and so does the paper. The water structure has moved (seeped) into the paper's structure aided by gravity in some way, the affinity of water for the paper in some way, the fine pores on the paper in some other ways. All such avenues have provided pathways welcoming water with

the available surrounding temperature and thereby providing the energy and allowing water's own structure to alter the structure of the paper. Result? The book is now deformed. The pages are swollen.

If the book is a bit unluckier the water could have had the opportunity to stand in between with the book closed with the water inside such that the pages got a longer time to play with the water. Imagine you forgot the book and only wanted to open it the next day. What would have happened then? Of course, you could have opened the book, yet few pages might have got stuck and as you forced your fingers through the stuck pages they would have made a crackling sound with the crackling of the pages ripping open apart! So now we see how important *time* is in the matter of structure. We will confine ourselves to the study of primarily *static structures* and to avoid complexity, we will start to study a simple liquid which is not even water, but much simpler!

1.7. Structure: Constituent and Energy: What is the 'Thing' made of? How is the Structure held together?

Structure of matter essentially manifest as its state. For instance, a matter can be most likely abundant as a solid or crystalline state, liquid and gas. Following the view of Kanad from early 6th BCE to Dalton and of late of Onsager's view in recent times matter is particulate. We will now try to build up a framework to describe and depict structure of this particulate matter correlating its interaction potential with its number density. In doing so we will invoke certain symmetry relations and conditions which we are slowly going to develop *a priori*. We will in fact, with our own way of reasoning develop and establish a description of matter in a liquid state and later demonstrate that its transition to solid/crystalline state can be described exactly with the descriptors that we have developed so far correlating the constituents of the matter with the energy that binds those constituents together. It is to be noted that the formalism that we will develop here will very well hold for liquid matter/colloids/soft-matter as well.

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Structure of liquid: $g(r) = e^{-\varepsilon/kT}$

Structure of liquid: $g(r) = e^{-\varepsilon/kT}$

L. Onsager, Chemical Reviews, 1933, 13, 73–89
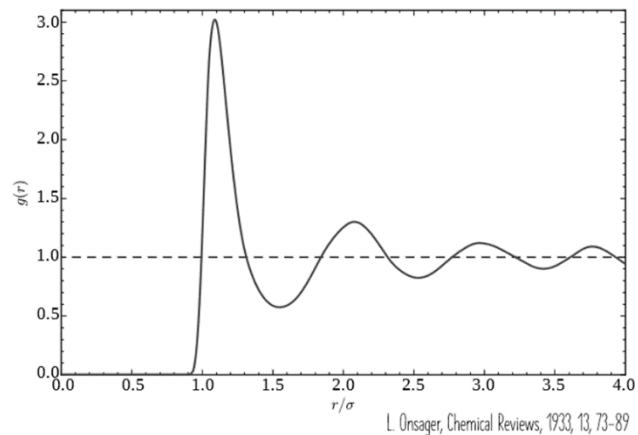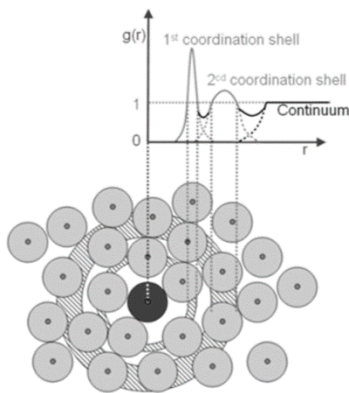
As a matter of fact, this formalism in principle with its own logic of correlation can be applicable to develop phase-transition models for any kind of matter with any number density and any topology of the constituents of the matter in question. Thus, we set out here to develop a general formalism for understanding states of matter as and when they manifest.

For the sake of brevity, in this description our thesis focuses on only one simple hypothesis: Formation of crystal/solid state of matter results from a phase-transition from the corresponding liquid state of matter. Such transitions can be described exactly in a framework, which we will develop now.

To establish our thesis, we start out with a brief introduction to states of matter and point to the forces that govern these states of matter. Our study will focus on liquids and how understanding liquids can lead us to study crystallization/solid state formation in general.

We will then give a very brief introduction to various models of liquids and their phase transitions and how these models coupled with the concepts of phase transitions can explain crystallization or solid formation in general.

1.8. On Structure of Liquids and their Transitions in the Context of Crystallization/Solid Formation:

To embark upon the idea of transitions in liquids we will invoke a hypothetical liquid-sand "analogy" to develop a structural particulate liquid model. At the outset, it should be emphasized that the liquid-sand "analogy" is extremely loose so to speak as there exist a host of microscopic theories describing sand (compactivity, arches criticality, etc.) and none of them bear on the statistical mechanics of the usual liquids and are not part of the discussion here. Now let us consider a beaker. A small 100 ml beaker. Let us imagine we put some sand grains (each grain having same size) in it so that it is quarter filled. Now we take a thin copper wire and we move the wire through it. It moves very easily and gives us a feel as if we were moving the wire thorough water. In fact, this quarter filled sand beaker can indeed be considered as a model of a liquid. Now we take the wire out and start pouring more sand into it till it is filled to its rim. We shake it and compress the sand in it until we cannot even put a single more grain into it. Now we try to do the same experiment. We take the wire and try to move it through the sand. This time the experience is different. We can barely even penetrate the surface. It feels like a solid surface! If, the wire is too thin, it even gets bent before it penetrates the surface. What we have essentially experienced through this simple thought experiment is phase-transition. We have converted a liquid state into a solid state by changing its packing density or packing fraction or volume fraction. In fact, going a step deeper we are faced with the question, is it possible to describe the structure of this liquid and to correlate the structural change with a measurable parameter? In fact, asking such a question leads us a step closer to the study of crystallization. In asking such question we tacitly consider crystallization to be a phase transition from a liquid state to a solid state. But before going that afar let us model our sand beaker simplistically. In case of quarter filled sand beaker (let us consider it as a liquid of interest) when we are moving the wire through the beaker, we are essentially exerting force on the constituents of that liquid. In doing so, the force is distributed across the beaker and we may see some ripples moving across the path of motion of the wire. In fact, what we are seeing is a structural transition taking place in that liquid as we perform this thought experiment. The question becomes, can we somehow 'measure' this structural transition and describe it with some functional that incorporates in its essence both the force/energetics and the structure? To do so, we resort to the conventional wisdom of coordination chemistry and invoke the idea of coordination number. [For a notion of bond orientational order parameters in liquids the reader may look up the work by: P.J. Steinhardt et al, Phys. Rev. B, 28, 784 (1983).]

1.9. Developing the Descriptors of Liquid Structure - Connecting Constituent and Energy - Mean Field Approximation and Radial Distribution Function g(r)

Now for the moment, we imagine that there is only a continuous medium. In that medium, there is a sand grain with a coordination number 6. Let us denote this grain with its corona of 6 grains as (L)L6. In assuming a coordination number 6 we are essentially tacitly assuming the easiest way to place other 6 grains around it so that they are in contact. Imagining that there is a continuous field (our liquid of sand) with the motion of the wire this moiety (L)L6 moves dynamically retaining its coordination number of 6 and its constitution. In fact, there is dynamics in the system and the force is dissipated in the dynamics of the system and the structure of the (L)L6 lait motif is maintained. We have in fact just discovered the subtle coupling of force/energy with dynamical structure of the liquid. So, the structure of the liquid can be described in terms of coupling of this corona of interest (L)L6 with the force field coupling the medium (liquid). We now expand our coordination environment of interest and we are in a position to describe the structure of the corona of our interest (L)Ln. Now the liquid of interest is composed of several such coronas of interests which are coupled by forces (energetics) of the medium. These forces essentially

depend on the individual nature of the constituents of the medium, and in this case: sand grains. Now as sand grains are essentially 'hard spheres', what we essentially have is a hard sphere liquid. The mean field force that any single particle of this liquid exerts on another particle at a distance 'r' is essentially coupled to the number density of the particles in this liquid and the interaction energy between two particles. This very concept also enables one to describe the structure of the liquid by describing the position of each such particles in the liquid and coupling it with energy of interaction, the potential of mean force of the liquid under consideration. Commonly this is known as the radial distribution function, denoted as g(r). It in turn, also describes the density fluctuation in the medium, with respect to a fixed point of reference. Now for this liquid one can write g(r) as,

$g(r) = e^{-\varepsilon/kT}$

where, k is the Boltzmann constant, T is the temperature and ε refers to the energy of interaction or more precisely the potential of mean force. Hence it is through this parameter, g(r), structure of a liquid and the energy of interaction couples with each other. This brings us to another important question of interest on what governs the nature of liquid and thus in turn can influence its phase-transition and crystallization. We note the following:

Nature of a liquid depends on its pairwise interaction potential (related to ε) between the particles/atoms. (Note: here for the sake of simplicity we are not considering the non-pairwise interactions which we though anticipate might be important for SOMs to be discussed in this review.)

On the ratio of attractive and repulsive interactions between the particles. [14, 15]

On the number density/volume fraction of the particles

Now for a deeper understanding let us expand the scope and consider some more model liquids beyond the imagined beaker of sand. The real-life examples of liquids are plenty. There is water, a molecular liquid. There is milk, yogurt, blood with proteins, paints. They are examples of complex liquids or colloids. Our experience says, milk can curd on addition of lime, blood can be sedimented into blood cells and proteins on spinning. A protein solution when followed with several protocols or treated with agents for 'salting out' can even crystallize. We also know that Hoffmeister early on arranged anions based on their interactions with proteins and their ability to form or destroy water structure ('chaotropy/cosmotropy') associated with the proteins.

1.10. On Nature of Liquids:

All such above observations on liquids serve as pointers to converge our thoughts to the aspects of liquids enumerated below. 1. Granular/particulate nature of liquids. 2. The nature of the liquid depends on the nature of interaction of the constituent particles. 3. The nature of the interaction between the particles can be 'tailored or tuned'. 4. Such tuning of interactions can help us modify the nature of the liquids. 5. Understanding the nature of interactions can enable us to describe and understand the properties of the liquid on a macroscopic scale. It is important to note that crystallization/solid formation can thus be understood as a phase transition of a liquid. Thus, the problem of crystallization can be modeled from the perspective of phase-transition and in doing so the model adopted by (colloid) chemists in the context of (colloidal) crystallization can be extended. We now describe several descriptions of visualizing liquids to bring home our desired goal to understand crystallization/solid formation.

The early efforts of visualizing liquid as a granular matter and applying the concepts of statistical mechanics to such particles or granules and using the potential of average forces in lines to the one as described above was first envisaged by Onsager. Based on this approach we describe following liquids which are manifestation of attractive and repulsive interactions.

1.11 Hard sphere liquids: In this type of liquid the constituents are hard spheres (HS). They are incompressible and when they collide with each other the pair potential is infinite. On the other hand, there is no attractive interaction component in this liquid. This model of liquid was proposed intuitively by J.- D. van der Waals as early as in 1873 which only contained hard or repulsive interactions. [17] Thus, they interact with the following pair potential.

$V = \infty$, $r < \sigma$

$= 0$, $r \geqslant \sigma$

Where r is the distance between the particles and σ is the diameter of the HS.

1.12. 'Soft' liquids or Polymer Colloid mixtures: It was as early as in 1935, that Kirkwood realized that HS liquids are too hard to realize. Real liquids need to have a 'soft' (long-range) attractive component in their pair potential. Thus, he wrote, "that probability distribution functions derived from rigid spheres can scarcely be applied to actual fluids, where the attractive forces play a dominant role in determining the form of the distribution functions." Realization of the attractive component in an otherwise repulsive hard sphere liquid can be attributed to Vrij. Elaborating further on the initial investigations of Asakura and Oosawa, Vrij explained that an attractive interaction component can be introduced in a colloidal liquid of hard-spheres by adding non-adsorbing polymers. In this framework an attractive interaction emerges due to the entropic stabilization of the system arising from the expulsion of polymers from the excluded/overlapping volume of colliding colloidal particles. Such attractive potential stemming from entropic stabilization is known as depletion interaction. The corresponding potential of mean force for such a system can be given as,

$V = \infty$, $r < \sigma c$

$= -\pi p - V_{overlap}$, $\sigma c < r < \sigma c + \sigma p$

$= 0$, $r > \sigma c + \sigma p$

Where r is the distance between the particles and σc and σp are the diameters of the colloid and polymers respectively.

It has been shown that in the polymer-colloid mixture, the activity of polymer serves as an equivalent parameter like that of inverse of temperature in an atomic liquid. [15, 21] We will briefly touch upon this aspect when we discuss phase transitions in such liquids in the next section.

1.13. Lennard-Jones liquid: This is another form of liquid which has both the repulsive component and the attractive component in its potential of mean force and is attributed to the early model of Lenard-Jones in 1924. The model holds good for noble gases and has been computationally modified to obtain various forms of liquid like 'weak liquid' and 'metastable liquid' as was proposed by Lekkerkerker in his seminal review on liquids. The 2n-n Lenard-Jones potentials used on various computer simulations to obtain such results have the following form:
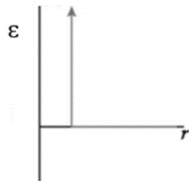
$V = 4 \in [(\sigma/r)2n-(\sigma/r)n]$

Where, $\in$, is the depth of the potential, σ is the diameter of the particle, r, is the inter-particle distance.
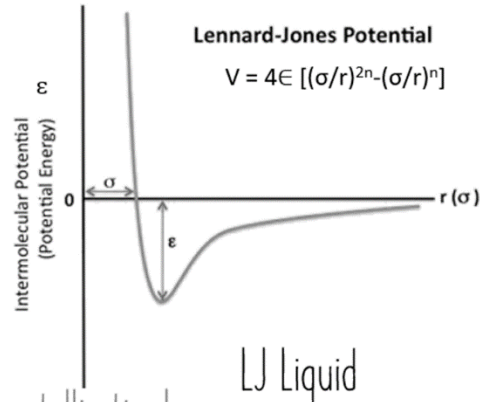
Liquid: $g(r) = e^{-\varepsilon/kT}$

Hard sphere potential:

This is the simplest potential, given by: $\varepsilon = \begin{cases} \infty, r \leq \sigma \\ 0, r > \sigma \end{cases}$

ε

r

HS Liquid

B. Widom, Science, 1967, 157, 375–382.
H. Lekkerkerker, Physica A: Statistical Mechanics and its Applications, 1997, 244, 227–237.

Lennard-Jones Potential

$V = 4 \in [(\sigma/r)^{2n}-(\sigma/r)^n]$

ε

Intermolecular Potential (Potential Energy)

σ

0

$r (\sigma)$

ε

LJ Liquid

Determine Crystallization!
In principle when there is a certain change in g(r) we can find ε.

1.14. Note on Virial Coefficient in the Context of Liquid Structure:

Using a value of n ranging from 6 -12, B2 the second virial coefficient, a measure of attractive interaction in the liquid can be obtained. B2 is indeed a fundamental parameter of a liquid and we will see later, that it gives us an input on the critical temperature of a liquid, and thus an idea on the phase-transition of the liquid as well. In fact, B2 can be treated as a measure of effective temperature of such systems giving in turn the measure of attraction in the liquid. It has been observed that for such Lenard-Jones liquids the value of second virial coefficient (B2) remains unchanged even if one changes n from 6 to 12. [15] This very near immutability in the value of B2 in fact is a key property that gives us a possibility to predict whether a liquid is close to critical temperature. In the present context of our review this observation becomes extremely important as crystallization can be considered as phase transition, whose onset can thus be predicted if we have an idea about B2. (See later section on SOMs and crystallization for the application of this concept.) As B2 represents a constant value at critical temperature, and depicts attractive interaction in the liquid, another possibility opens up. How about the possibility of the existence of a liquid, the particles (say hard-spheres) of which, are bound to one another by an infinitesimally thin range of attraction but with an infinitely deep attraction? Baxter's hard-sphere model with infinitesimally thin and infinitely deep attractive well, explores that possibility.

1.15. Adhesive Hard Sphere (AHS) Liquid model of Baxter:
Baxter introduced the pair-wise interaction incorporating the above features in an adhesive hard sphere (AHS) model. He introduced a new parameter, the 'stickiness parameter' to represent the adhesive strength of the spheres in the liquid. A low value of the parameter implied strong adhesion. He further correlated this stickiness parameter with B2 and thereby opening up a window of experimental eyes to quantify this stickiness. τ. Thus the pair potential envisaged by Baxter becomes,

$V = \infty$, $r < \sigma$

= ln 12τΔ/(σ+Δ) σ ⩽ r ⩽σ+Δ

= 0, r >σ+Δ

Where Δ is the infinitesimally thin width of the potential and is applied at the limit

 Δ→0.

Where, B2 = VHS (4-1/τ)

VHS, being the volume of the hard sphere. Thus, in fact, the stickiness parameter in turn is a measure of effective temperature of the system and can be measured experimentally from B2. [Although we are aware of the limits of AHS at higher virial coefficients. See for instance, G. Stell, J.Stat Phy 63 1203 (1991).] However, in the context of study of crystallization studies, a range of B2 has been proposed experimentally where phase transitions thus crystallization can occur for a Baxter type model. Can you now think and tell, can any liquid be approximated as a Baxter liquid? But, as of now we ask: can these interactions be rendered more specific or as patches?

1.16. Patchy particles: In this model, instead of a thin attractive isotropic stickiness of the particles of the liquid, every particle is modeled with a 'patch' of attraction and an isotropic repulsion. The patch has an attraction which is both orientation and position dependent. The repulsion component can be a simple Lenard-Jones potential as described above. The elegance of this model lies in its ability to connect the microscopic details of the structural components of the 'liquid' i.e., of the particles to its macroscopic thermodynamic properties (phases). This model has been applied in understanding SOM structure formation by Roy and Kegel.

1.17. Mapping Thermodynamics and Structure: Criticality, g(r) and Energy of Constituents of Liquid as it Undergoes Phase-transition/Solid Formation or Crystallization

As we inch our way toward understanding crystallization, we put forward our thesis of this discussion. Crystallization/solid formation (in any matter with any constituent) can be considered as a phase-transition from a liquid/soft-matter state to crystalline/solid state. But to clearly understand and explain our thesis we revert back to our sand grain model of the liquid we proposed earlier. We ask what happens to this model at the point of phase-transition so that we can understand crystallization better. When a liquid undergoes phase transition, structurally speaking, some changes ought to take place in its g(r), the parameter we described earlier giving us an idea on the arrangement of particles or atoms or granules in the liquid. A periodicity has to be introduced in the structure. In other words, g(r) becomes a periodic function. We have also seen that g(r) can be related to the density of the liquid. In fact, there is a relation that couples g(r) with the isothermal compressibility of the medium, that was derived by Orstein and Zerenicke. Such a relation directly maps thermodynamics with the structure. So, what happens to the liquid as it undergoes phase transition or let us put it more specifically when it co-exists with its own solid and vapor phase? It can be shown three critical phenomena take place that are essentially thermodynamic which captures the change in structure of the liquid. 1. The compressibility becomes very large near the critical point which describes the thermodynamics of the system near or at critical point. 2. The inhomogeneities in the structure of the liquid becomes very high at the critical point so much so that the fluctuations become very high and that leads to the emergence of 'critical opalescence', (high scattering intensity) indicative of the induction of a structural transition taking place in the 'liquid' at the critical point. 3. The specific heat capacity at constant volume (Cv) suffers a discontinuity with temperature as the

system undergoes phase transition and finally it settles around a stable value of 3/2 NkT as the system has solidified. Thus, it is reasonable to expect that these phenomena will manifest during or at the point of crystallization, and the current literature indicates the existence of a dense liquid phase in the matter of crystallization. Note: The two-step nucleation theory essentially captures this essence. It says that a liquid phase precedes crystallization and some critical fluctuations in that liquid sets in crystallization. In proteins the same model has been suggested where a LLPT (Liquid-Liquid Phase Transition) is said to be the key that leads to crystallization. With our present thesis, we propose exactly the same phenomenon to be happening in the crystallization or solid formation in any type of matter.

1.18.   Our thesis: Crystallization/solid formation of any matter is a phase-transition of its liquid state to solid-state.
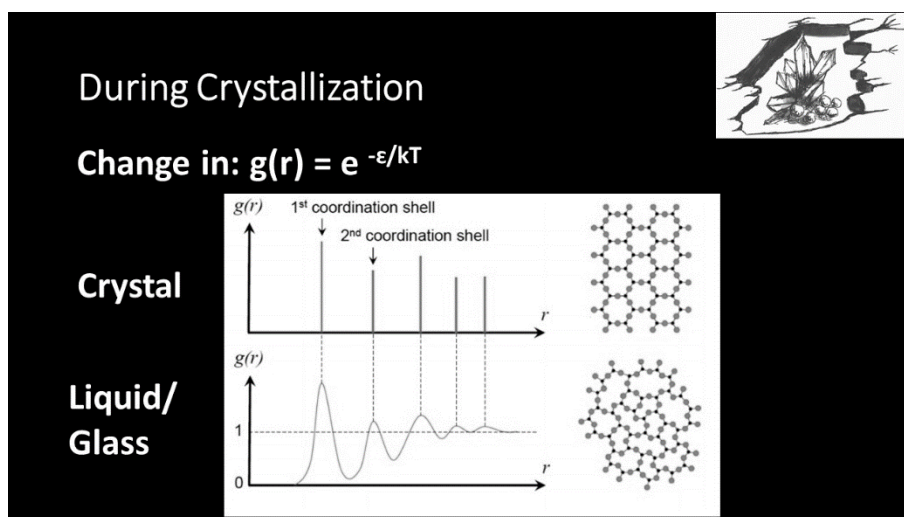
In the crystallization/solid-formation of any matter we propose that there are two essential steps. 1. A molecular phenomenon: In a rather rapid time-scale first the molecular constituents are formed, which is likely to be an ultra-fast chemical process. 2. Such a process will be followed by a relatively slow 'beyond the molecule' or a supramolecular phenomenon: In the second step, the liquid state so formed by the nascently formed constituents undergoes phase-transition to form crystalline/solid state.

From this formalism or description, it so appears that if we 'KNOW' the interactions between the constituents we can construct any liquid. We now further ask a more ambitious question: what might be the possible way to describe the structure of a crystal/liquid? What we would need for such a description? What would be the formalism to address such a question?

We are in fact dealing with Static Structure.

Reactivity refers to Dynamic Structure, just that we note.

We will next see how we can determine structure of any object with scattering.