A structural investigation into the complexity of mesoporous silica crystals – From a view of curvature and micellar interaction to quasicrystallinity

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A structural investigation into the complexity of mesoporous silica crystals

From a view of curvature and micellar interaction to quasicrystallinity

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To my dear Mengmeng
Abstract

Mesoporous silica crystals have a large variety of structures mainly due to the versatility of their structure template. The configuration and the chemical state of the templating micellar surfactants, together with the kinetic process of silica will determine the final outcome of the synthesis. Increasing the understanding of the complex formation processes involved will enable a possibility to fine tune the material for specific uses, today focused into the fields of photonic crystals, drug delivery, catalysis and separation technology.

In this thesis emphasis is put on (1) increasing the understanding the formation mechanism yielding the different species of mesoporous silica crystals through an in depth study of quasicrystallinity (2) Characterization and description of the structural complexity through various characterization techniques and also by studying the kinetic structural transformation phenomenon related to the minimal G- and D-surfaces. (3) The structural studies of the versatile surfactant liquid crystals for establishing a thermodynamically stable basis to evaluate the kinetic mesoporous silica growth processes. Furthermore the thesis both enlightens the possibilities of and contributes to the development of electron microscopy characterization techniques.

In these studies, electron microscopy is largely employed in the characterization to give a thorough picture of the mesoporous structures. This is combined with the sample preparation techniques cross-section polishing and ion slicing. Low voltage scanning electron microscopy is utilized for studying the surfaces and cross-sections of various materials at the limit of the resolution. Here, a deep understanding of the electron beam-material interaction is used for a better interpretation of the detected signals. Transmission electron microscopy is combined with electron crystallographic reconstruction to yield a three dimensional structural model. For determination of the quasicrystallinity level for a structure of dodecagonal tiling, revealed in the scope of this study, a phason strain analysis was made.
List of Papers

The following papers, referred to in the text by their Roman numerals, are included in this thesis.

PAPER I: **Dodecagonal tiling in mesoporous silica**
DOI: [10.1038/nature11230](https://doi.org/10.1038/nature11230)

PAPER II: **Bicontinuous cubic mesoporous materials with biphasic structures**
DOI: [10.1002/chem.201101831](https://doi.org/10.1002/chem.201101831)

PAPER III: **Mesopore Generation by Organosilane surfactant during LTA zeolite crystallization, investigated by High-resolution SEM and Monto Carlo simulation**
DOI: [10.1016/j.solidstatesciences.2010.04.022](https://doi.org/10.1016/j.solidstatesciences.2010.04.022)

PAPER IV: **Cracking mechanisms of clay-based and GCC-based coatings**

PAPER V: **A novel SEM cross-section analysis of paper coating for separation of latex from void volume**

PAPER VII: Structures of the C$_{14}$GlutANa surfactant liquid crystals
Changhong Xiao, Keiichi Miyasaka & Osamu Terasaki, in manuscript

Reprints were made with permission from the publishers.

Publications not included in the thesis.

PAPER I: Nano pores evolution in hydroxyapatite microsphere during spark plasma sintering
DOI: doi:10.2298/SOS1101039L

PAPER II: A review of fine structures of nanoporous materials as evidenced by microscopic methods
Zheng Liu, Nobuhisa Fujita, Keiichi Miyasaka, Lu Han, Sam M. Stevens, Mitsuo Suga, Shunsuke Asahina, Ben Slater, Changhong Xiao, Yasuhiro Sakamoto, Michael W. Anderson, Ryong Ryoo & Osamu Terasaki, submitted

PAPER III: Highly heterogeneous polycrystalline materials with engineered structural hierarchies
Bin Qian, Changhong Xiao, & Zhijian Shen, submitted
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## Abbreviations

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<th>Full Form</th>
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<tbody>
<tr>
<td>$C_{14}GlutANa$</td>
<td>Sodium N-Myristoyl-L-Glutamate</td>
</tr>
<tr>
<td>$S_2C_{14}$</td>
<td>(S)-(1-tetradeylcarbamoyl-2-phenylethyl)-dimethylethylammonium bromide</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>AMS</td>
<td>Anionic surfactant templated mesoporous silica</td>
</tr>
<tr>
<td>APES</td>
<td>(3-aminopropyl)triethoxysilane</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered electron</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>CSDA</td>
<td>Co-structure directing agent</td>
</tr>
<tr>
<td>CTF</td>
<td>Contrast transfer function</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier transform</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MTP</td>
<td>Multiply-twinned particle</td>
</tr>
<tr>
<td>PE</td>
<td>Primary electron</td>
</tr>
<tr>
<td>PSF</td>
<td>Point spread function</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small angle X-ray scattering</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethyl orthosilicate</td>
</tr>
<tr>
<td>TMB</td>
<td>Trimethylbenzene</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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1. Introduction

1.1 Mesoporous silica and AMS

1.1.1 formation of mesoporous silica

The *meso* in mesoporous silica means the pore size is in the range of 2nm to 50nm. The porous structure is templated by surfactant, which has a hydrophobic tail and a hydrophilic head group. Due to their amphiphilic nature, the surfactants self-assemble in polar solutions such as water to form micelles. Pure surfactant-water system could form micelles when the surfactant concentration is higher than the *critical micelle concentration* (CMC). However, mesoporous silica material can be synthesized at surfactant concentration lower than CMC by the assistance of the silica oligomers. This process is commonly nominated as cooperative self-assembly, in which the silica source also plays a critical role, in addition to the *structure directing agent* (SDA) of surfactants, in affecting the final structure. Thus unlike the thermodynamically stabilized liquid crystal structures of surfactant/water system, the formation of mesoporous structures involve a kinetic process.

Depending on the surfactant used, the synthesis strategy varies according to the feature of the head group. For the ionic surfactants, the electrostatic interaction plays the major role for the interaction between the inorganic precursors and the surfactant micelles. Depending on whether the surfactant (S) head group is anionic or cationic, synthesis condition is modified so that the inorganic precursors (I) have the opposite charge to surfactant head group in order to cover and condense on surface of the micelles. These synthesis route are identified as $S^+I^-$ or $S^-I^+$. For the case where S and I have the same charge, other counter-ions are involved as charge compensation species, such as $Cl^-$ or $Na^+$ ($X$). The synthesis route in this case can be represented as $S^+X^-I^+$ or $S^-X^+I^-$. For non-ionic surfactants, H-bond or dipole takes over to be the main reaction force between the inorganic species and surfactant template. All these synthesis routes are describe in Figure 1.1.
1.1.2 Anionic surfactant templated mesoporous silica (AMS)

In the family of mesoporous silica templated by various kinds of surfactants, AMS is one branch full of interesting structures. One important feature of AMS is the use of co-structure directing agent (CSDA) as the bridge between the surfactant headgroup and the silica source. The CSDA differs from the counterions in $S^+X^-I^+$ or $S^-X^+I^-$ synthesis route in that it’s not just the charge compensation between the surfactant headgroup and the silica precursor with same charge. It is designed to have one side positively charged and the other made of silyl eithers. The positively charged side brings it to surround the negatively charged micelles by coulomb force while the other side hydrolyses to form Si-O-Si chains with silica precursors in solution. This synthesis route makes it possible to get ordered mesoporous silica in both acidic and basic conditions by using anionic surfactant. One typical CSDA is 3-aminopropyltrimethoxysilane (APS) and the interaction with the surfactant can be see in Figure 1.2.

Another advantage of using CSDA is that, after extraction of the surfac-
Figure 1.2: (a) The CSDA of APS and (b) its interaction with anionic surfactant

In addition to the synthesis and application advantages introduced by using CSDA, partially hydrolyzed CSDA surrounding the micelles also brings more flexibility to the structure of micelles, allowing various kinds of structure to be synthesized using just one kind of surfactant [26]. With several kinds of structure in one synthesis diagram and close to each other in terms of synthesis condition, structure transformation can be studied carefully and the mechanism can be discussed in more detail [41].

1.2 Structural characterization of porous materials

The morphology as well as the arrangement of pores are the two main structural information that describe the porous materials. A direct observation is intuitive, but with different constrains: only surface features can be seen by scanning electron microscope (SEM), while transmission electron microscope (TEM) images give merely 2D projected view of the 3D structures. Some constraints can be compensated by information in reciprocal space that reveals the crystallographic information of the materials, for this, a coherent beam of x-ray or electrons is needed.
1.2.1 Low voltage Scanning Electron Microscope

SEM has long been used as a method to rapidly gather information such as particle size and crystal morphology. This is due to the microscope’s long depth of focus and that it’s relatively easy to operate compared to TEM. However, unlike an optical microscope which mimic an extended human eyes, electron microscopes require an understanding of the electron-matter interaction, in order to correctly interpret the images and to get the most information from the microscopes.

Scattering of electrons and interaction volume

Depending on whether the incident electrons lose their energy during interaction with matter, the scattering of electrons are categorized into elastic scattering and inelastic scattering. Elastic scattering results from the coulombic interactions between the primary electron (PE ) and both the nucleus and electrons of the material, so that the PE can change direction without the loss of energy. Inelastic scattering contains several kinds of interactions that cause the PEs to loose their energy: 1) plasmon scattering where the waves in the conduction band are excited, 2) phonon scattering where the atoms inside solid are vibrated, 3) inner shell excitation which causes the jump and relaxation of inner shell electrons, producing X-Ray or Auger electron.

The possibility of one electron to be scattered depends on the atomic number of the material and the electron energy. Larger atomic number or lower electron energy could increase the possibility of scattering, by effect of more concentrated electrical field and easier-to-change electron trajectory respectively. A mathematical function helps to describe quantitatively the possibility of an electron being elastically scattered to an angle greater than $\phi$:

$$Q(> \phi) = 1.62 \times 10^{-20} \frac{Z^2}{E^2} \cot^2(\phi/2)$$  \hspace{1cm} (1.1)

where $Q$ is called the cross section for elastic scattering. We can see that $Q$ is proportional $Z^2$ and reversely proportional to $E^2$.

Inelastic scattering does not happen independently but together with elastic scattering in the electron trajectory, thus the dependence of energy loss to atomic number and electron energy have the similar trend to that of scattering cross section. By various ways the kinetic energy is lost gradually until the electron is rested with only thermodynamic energy, and the energy loss rate is described as the energy loss $dE$ with distance travelled $ds$:
\[
\frac{dE}{ds} \text{ (keV/cm)} = -2\pi e^4 N_0 \frac{Z\rho}{AE_i} \ln \left( \frac{1.166E_i}{J} \right) \tag{1.2}
\]

\[
J(\text{keV}) = (9.76Z + 58.5Z^{-0.19}) \times 10^{-3}
\]

where \(e\) is the electron charge, \(N_0\) is the Avogadro’s number, \(Z\) is the atomic number, \(\rho\) is the density \((g/cm^3)\), \(A\) is the atomic weight \((g/mole)\), \(E_i\) is the electron energy \((\text{keV})\) at any point in the specimen, and \(J\) the average loss in energy per event \([6]\). The above equation is only valid for the energy range from approximately 5keV to 50keV. For low beam energy, it’s found the number of processes contributing to the energy loss decreases, thus \(J\) is replaced by another form:

\[
J^* = \frac{J}{1 + (kJ/E)} \tag{1.3}
\]

\[
k = 0.731 + 0.0688\log_{10}Z
\]

By both scattering effects, the incident electrons will penetrate a hemisphere-like region inside the material before they stop. This volume of penetration is called interaction volume \([\text{Figure 1.3}]\). It is the volume where the detected signals such as X-ray come from. A simple representation of interaction volume is the electron range, which is defined as the radius of a hemisphere that contains a specified fraction of the electron trajectories, for example 90%. 100% is not used here since by simulation the last 10% extends a significant volume, where not much scattering is happening. The electron range is strongly related to the energy loss rate in Equation \((1.2)\), and it decreases almost linearly with decreasing beam energy at energy range \((\gtrsim 1.0\text{keV})\), while reaches a limit for low energy range \([29]\).

**Back scattered electron (BSE) and secondary electron (SE)**

The difference between BSE and SE comes from their origin of generation. The BSE are the primary beam electrons that escape from the entrance surface after numerous elastic scattering events to cumulatively change the trajectory directions backwards, while SE normally refers to the electrons from the weakly bound conduction bond in metals or the outer shell valence electrons of semiconductors and insulators, which receive sufficient kinetic energy to be ejected and escape from the specimen surface. The energy distribution of BSE is not far from the energy range of incident electron beam, as the inelastic scattering involves relatively small scattering angle and contribute little to the backscattered signal. The incident electrons that are not backscattered
outside the specimen surface undergo various inelastic scattering process and eventually rest in the solid, or become conduction electrons in metal. The energy distribution of SE is concentrated below the energy of 10 eV (more than 90% of the SE) although the conservative definition is below 50 eV. Considering Equation (1.2) where the energy loss rate is reversely dependent on the kinetic energy, the low energy of the SE makes it strongly attenuated with distance travelled, resulting in an electron range and escape depth as shallow as in nanometer order (~1 nm for metals and ~10 nm for insulators). Thus SE is mostly utilized for the surface morphological information.

**Z dependence**

An important feature of BSE is its dependence on the atomic number, so that the contrast by BSE can be used to illuminate the element distribution in a
composite material. This dependence comes from the elastic scattering process which is quantified by the backscatter coefficient $\eta$, defined as $\eta = \frac{n_{BSE}}{n_B} = \frac{i_{BSE}}{i_B}$, where $n_B$ is the number of beam electrons incident on the specimen and $n_{BSE}$ is the number of backscattered electrons. The dependence on the atomic number $Z$ can be fitted by:

$$\eta = -0.0254 + 0.016Z - 1.86 \times 10^{-4}Z^2 + 8.3 \times 10^{-7}Z^3$$

(i.e. the larger atomic number will normally have a higher BSE yield.

The $Z$ dependence is weakly affected by the impacting energy at conventional beam energy (e.g. >5keV), however for low beam energy, the yield of BSE is often affected by the contamination layer accumulated on the sample surface, making BSE not truly come from the material. Due to the same reason of contamination on the surface, the dependence of SE on the specimen composition is not easy to determine.

**Angular dependence of BSE**

The dependence of BSE on sample tilting angle is dominant especially at high angles (e.g. >45°) and can be fitted by the function:

$$\eta(\theta) = \frac{1}{(1 + \cos \theta)^p}$$

(1.5)

, where $\theta$ is the tilting angle of specimen surface normal relative to the incident beam axis, and $p = 9/\sqrt{Z}$ . This behaviour of $\eta$ versus $\theta$ is because tilted surface increases the possibility for the electrons with less angular deviation to escape, thus increasing $\eta$. A graphic representation of the formula is shown in Fig. 1.4(a)

As the backscattered electrons have high kinetic energy and are merely slightly affected by the bias applied on the detector, only the BSE that escape in the direction of the detectors are collected. Knowing the angular distribution of the BSE in addition to the position of the detector is thus necessary to correctly explain the contrast on the images. For this not only the elastic scattering process needs to be considered, but also the trajectory of the electrons. Although the cross section for elastic scattering of higher angle is smaller as shown in Equation[1.1] the trajectory to escape at a lower deviation angle is longer, making the angular distribution of BSE concentrated around the incident beam axis. At normal incidence, the angular dependence can be approximated by:

$$\eta(\phi) = \eta_n \cos \phi$$

(1.6)
where \( \phi \) is the angle defined by the surface normal \( \mathbf{n} \) and the escape direction \( \mathbf{m} \), and \( \eta_n \) is the value along the normal vector \( \mathbf{n} \). A graphics representation of the formula is shown in Fig. 1.4(b). For tilted surfaces, the angular distribution is concentrated in the forward direction of the primary beam for the same reason as aforementioned sample tilt dependence.

**Figure 1.4:** (a) The dependence of BSE yield of Silicon \((Z = 14)\) on the tilting angle of the specimen surface and (b) the angular distribution of BSE, where the length of the arrow in the figure represents magnitude of \( \phi(\theta) \)

**Angular dependence of SE**

The angular distribution of SE is relatively less dominant in the image formation process, since the bias applied on the detector (a few hundred volts) would drastically change the trajectory of SE after it escapes from the sample surfaces. The theoretical prediction of the angular dependence of SE from polycrystalline surfaces can be approximated by a cosine function similar to that of BSE, as depicted in Fig. 1.4(b) [42]. Unlike that of BSE, the angular distribution of SE is independent from the incident beam direction, because of the isotropic generation of the SE by inelastic scattering. However, the SE yield is sensitive to the sample tilt, and the relationship could be easily derived considering the escape depth of the SE (Fig. 1.5): assuming the escape length to be constant \( h \) in the direction of surface normal, for normal incidence, the escape region is a cylinder of the beam radius \( d/2 \) and height \( h \), *i.e.* volume \( V(0) = (\pi/4)d^2h \), while for inclined surface, the escape region is a slanted cylinder with height \( h \) (perpendicular to the surface) and base of cross section area \( (\pi/4)(d/sin\phi) \) \( \phi \) is the incident angle with respect to the surface normal), *i.e.* escape volume of \( V(\phi) = \pi(d/2)^2(h/cos\phi) \). This could give a tilt dependence function of the SE yield as [19]:

\[
\eta(\theta) = \frac{1}{\cos \theta}
\]
\[ \delta(\phi) = \delta / \cos \phi \]  

(1.7)

from which we could see that a higher tilted surface gives larger SE yield, which could result in a brighter contrast in the SE images.

\[ \delta_T = \delta_p + \delta_B \eta \]  

(1.8)

Figure 1.5: The graphic description of the SE yield \( \delta \) dependence on the sample tilt

Energy dependence and SE1, SE2

In order to understand the energy dependence of SE yield \( \delta \), we need to consider the two kinds of processes contributing to the total SE: primary beam and BSE. The primary beam pass through the specimen surface and generate SE within the escape distance. Those SE are designated \( SE_1 \) and they are a high-resolution signal that preserve the lateral spatial distribution of the focused primary beam. The BSE, when they reach the region of escape depth, can also generate SE, which is designated as \( SE_2 \) (Fig. 1.3). The lateral distribution of \( SE_2 \) follows that of BSE which makes \( SE_2 \) a low-resolution signal. The total secondary electron coefficient \( \delta \) is composed of two parts, \( \delta_p \) and \( \delta_B \), corresponding to \( SE_1 \) and \( SE_2 \):

They efficiencies of BSE and PE in generating SE are both dependent on energy, which ultimately determine the energy dependence of \( \delta \). The parameter \( \beta \) is used to describe the dominance of BSE and PE in generating SE, with \( \delta_B = \beta \eta \delta_p \). A \( \beta \) value larger than 1 indicates a higher efficiency of BSE while a lower than 1 value means PE is more efficient. Experiments conducted at incident energy larger than 1 keV found that he \( \beta \) value is of a few
unities \[61\]. This could be understood as BSE has a wider angular distribution and a longer trajectory within the escape region of SE, also compared to PE the lower-energetic BSE encounters more inelastic scattering, as described in Equation (1.2). However, at low incident energy, things become different, when the penetration depth of the PE is comparable to the escape depth. The higher emergence angle of BSE plays no role as they could not offer enough kinetic energy for SEs to escape from the surface. The value of $\beta$ in this case is smaller than unity, and is dependent on the material of interest. For light element such as carbon $\beta$ is close to 0.5 while for heavier element like gold, this value can approach 0.9 \[11\].

![Figure 1.6: Graphic representation of a typical energy dependence of the SE yield $\delta$, the vertical dashed lines point out the critical energies where the SE yield equals unity.](image)

The detection of BSE and SE

The energy-dependent efficiencies of the BSE and PE on producing SE would then contribute to the energy dependence of $\delta$ especially at low energy range. As discussed above, at very low voltage, the PE dominates in producing SE, thus $\delta$ increases with increasing incident energy, due to the increased kinetic energy that PE can offer to the electrons close to sample surface. At some point the BSE joins to contribute and effectively each incident electron could result in more than one out-coming SEs, \textit{i.e.} $\delta > 1$. However, as the penetrating depth continue to increase, less BSEs are able to reach the sample surface, \textit{i.e.} a decreasing $\eta$, and also the higher-energetic PE encounters less scattering within the escape distance. From Equation (1.8) we could imagine a declining $\delta$. As $\eta$ is weakly dependent at conventional beam energy (\textit{e.g.} > 5keV), and
Figure 1.7: The graphic illumination of the (a) BSE detector, (b) In-lens detector and (c) Everhart Thornley detector

at this energy range the BSE dominates in generating SE, the dependence of $\delta$ on beam energy becomes weak too. A conceptual graphic description on the energy dependence of $\delta$ can thus be depicted in Fig. 1.6.

During collecting electron signals, a proper separation of BSE and SE can help specify the information of the materials reflected from the detected signals. BSE is normally enhanced by a dedicated detector located on top of the specimen (Fig. 1.7(a)), as more BSE can be detected as reflected by Equation (1.6) and Fig. 1.4(b) A separation of SE is realized by utilizing its low energy, which means their trajectory are easy to be directed by external electronic or magnetic field. A bias on the sample stage can differentiate electrons with different energies, pushing low-energy SEs into dedicated in-lens detector (Fig. 1.7(b)), forming high-resolution images with “pure” surface information [2], while the higher-energetic BSEs are weakly affected and follow their initial trajectory, so that they contribute relatively much less than SEs in the image. Secondary electrons can also be generated when BSE hit the
pole pieces, which act as noise in the image. This kind of SE is commonly named as $SE_3$ (Fig. 1.7(e)). Most conventional SEM have the lateral detector on the side of the sample chamber, called Everhart Thornley type detector (Fig. 1.7(c)). It detects BSE coming to it, and a positive bias is applied on the front grid of the detector that can attract SE. Due to its lateral location, more electrons could reach the detector if they come from surfaces facing it, while the trajectories of electrons coming from surfaces facing oppositely are largely blocked. This feature helps to enhance the three-dimensional appearance of the images, similar to a rough surface obliquely illuminated by light, and is useful in interpreting the topographical contrast from wells and protrusions on sample surfaces.

**The lateral resolution**

Similar to the optical microscope, where the Point Spread Function (PSF) is used to describe the convolution that point light source needs to produce the ultimate image, thus serves as a detailed description of the resolution. In the case of SEM, the PSF is described by the radial distribution of the emitted SE, and is considered to be composed of two Gaussian functions $J_P(r)$ and $J_B(r)$ at normal incidence [10], corresponding to the $SE_1$ and $SE_2$ respectively:

$$J(r) = I_P \delta_p (\pi \sigma^2_P)^{-1} \exp[-(r^2/\sigma^2_P)] + I_B \delta_B (\pi \sigma^2_B)^{-1} \exp[-(r^2/\sigma^2_B)]$$  \hspace{1cm} (1.9)

where $\sigma^2_P \sim d^2/4 + s^2$ and $\sigma^2_B \sim \sigma^2_P + R^2/4$, $d$ is the incident spot diameter, $s$ is the escape depth of the $SE$ and $r$ the range of PE.
The contribution of $SE_1$ to the Equation (1.9) is a sharp function while that of $SE_2$ is a broaden distribution with low amplitude at conventional incident energy (e.g. 10 keV) (Fig. 1.8). A rough simplification can be made so that a conceptual idea can be derived from Equation (1.9): at $r = 0$ where Gaussian function has the maximum value, the ratio of the $SE_1$ and $SE_2$ contribution to the $J(r)$ is $J_P(0)/J_B(0) \sim (\delta_P/\delta_B)(\sigma_B^2/\sigma_P^2) \sim (\delta_P/\delta_B)((\delta_B^2 + R^2/4)/(d^2/4 + s^2))$. At conventional incident energy ($\sim$ 10 keV), as described in the last paragraph, the $\delta_P$ and $\delta_B$ possess value of the same order, and the $R$ in micrometer range is way larger than the $d$ and $s$ in nano-meter range, thus the ratio can be simplified to $(R/d)^2$, which is in the order of 10$^3$ (i.e. $\mu m/nm$). A smaller $d$ would increase the value of this ratio, meaning a sharper radial distribution, which is in accord with the common sense that a smaller spot size of the incident beam would enables images with higher resolution.

At low impacting energy (e.g. $< 0.5$ keV), this simplification is not valid since the $R$ value decreases to be comparable with $s$. The ratio of $\sigma_B^2/\sigma_P^2$ approaches unity and $J_P(0)/J_B(0)$ is approximately governed by $\delta_P/\delta_B$ instead. Thus the resolution is not just determined by the instrument’s beam spot size but are sensitive to the sample compositions as well as the operating energy.

**Low voltage electrons**

What baffles material scientist most during SEM operation is the charging problem. Although other complementary methods are available such as carbon coating, they will contaminate the original surface thus it’s difficult or even impossible see the fine structures on surfaces of insulating materials. The charging problem can be solved if the landing electron energy can be as low as the critical energy, where the number of electrons emitted is equivalent to the number of incident electrons (i.e. $\delta = 1$) (Fig. 1.6), then there is no accumulated electrons on the surface of the materials even if the material is not conductive. However It does not mean that lower lading energy is always better for the image quality, as we need to consider the signal/noise ratio at low energies. The emitted electrons can also be more than the incident electrons (i.e. $\delta > 1$) at landing energy range between the two critical energies $E_{C1}$ and $E_{C2}$ (Fig. 1.6), which may lead to accumulated positive charge on sample surface. How the positive charge affects the image contrast needs a future experimental investigation [1].

Different materials have different energy dependence of the electron yield $\delta$, most of them have critical energy of lower than 1 keV and some may be too low energy which cannot be achieved by commercially available SEM. However, at least for the insulating material of silica, the development of HRSEM has passed its threshold of $E_{C2}$, which makes the observation of its fine struc-
ture possible without charging problem. This breakthrough extends the power of HRSEM into the field of mesoporous silica materials, where the mesopore features are the main focus and a fast and intuitive characterization of them are eagerly desired [66].

Low resolution will normally come together with the low voltage, as the chromatic aberration of electron lenses depend on the ratio $\frac{\Delta E}{E}$ [73], where $\Delta E$ is the energy spread and $E$ is the beam energy. With $\Delta E$ hard to decrease, large $E$ is the only way for a higher resolution. To solve this contradiction, some SEM applies a negative bias on the sample stage, so that the high-energy electron beam will be decelerated just above the sample surface, resulting in a low landing energy while a moderately high $E$ within the lens, thus a high resolution at low landing energy.

Following the low landing energy is the low yield of electron signal, which may result in low single/noise ratio. To settle this problem, low working distance is used in practice and semi in-lens objective lens is used to apply magnetic field on the sample surface to attract more SE from it (Fig. 1.7(b)). The SE signal attracted into the lens column is then amplified by a signal enhancer so that more secondary electrons can be seen by the detector [2].

1.2.2 Transmission electron microscope (TEM)

The instrument

The TEM instrument is composed of roughly three parts: the illumination system, the objective lens with stage, and the detecting system. The illumination system consists of Electron source and condenser lens. Several types of electron sources are available: thermionic emission source where heat is applied for electrons to overcome their energy barrier to come out of the filament; Field emission on the other hand utilize the ambient electric field to lower the energy barrier, and sharp point of the electron source is also designed to increase the strength of the electric field. Compared to thermionic emission, field-emission sources produce more monochromatic electrons, but thermionic sources can give larger electron emission. Since pure field-emission source (often called “cold field emission”) requires pristine environment, i.e., ultra high vacuum, it’s quite common that both heat and electric field are used, and this is called “Schottky” emitter. Condenser lens concentrates light from the electron source. Objective lens is set to surround the sample, and is used to focus the electron beam through the object and form images and diffraction patterns, which are in turn magnified by the intermediate lens and projector lens of the detecting system and are finally recorded by CCD or film. The lens system is shown in Fig. 1.9.
Figure 1.9: Graphic description of lens system of TEM [73]
Weak-phase-object approximation

All the images recorded are the magnified electron waves transmitting the specimen. If we assume the incident electron beam is coherent and the wave amplitude to be unity, the existing wave can be presented as

\[ f(x,y) = \exp(i\phi_t(x,y)) \quad (1.10) \]

where \( \phi_t \) is the phase of electron wave after transmitting specimen of thickness \( t \).

To find out the dependence of \( \phi_t \) on the specimen, we need to think about the electron interaction with specimen. Electrons in specimen would experience the potential of the specimen \( V(x,y,z) \). As the electron wavelength can be expressed as

\[ \lambda = \frac{h}{\sqrt{2mE}} \quad (1.11) \]

where \( E \) is the energy of the incident electron. In vacuum, \( E \) is equal to the kinetic energy of electrons \( \left( \frac{h}{2\pi} \right)^2 \frac{k^2}{2m} \). In the crystal, where an electrostatic potential \( V(x,y,z) \) exists, the electron has the energy of \( E - eV(x,y,z) \), and the corresponding wavelength in crystal is

\[ \lambda' = \frac{h}{\sqrt{2m(E + eV(x,y,z))}} \quad (1.12) \]

Thus after the electron has passed a slice of material of thickness \( dz \), the electron experiences a phase change of

\[ d\phi = 2\pi \frac{dz}{\lambda'} - 2\pi \frac{dz}{\lambda} \]

\[ = 2\pi \frac{dz}{\lambda} \left( \frac{\sqrt{E + eV(x,y,z)}}{\sqrt{E}} - 1 \right) \]

\[ = 2\pi \frac{dz}{\lambda} \left( \left( 1 + \frac{eV(x,y,z)}{E} \right)^{\frac{1}{2}} - 1 \right) \quad (1.13) \]

with \( eV(x,y,z) \ll E \)

\[ d\phi \simeq 2\pi \frac{dz}{\lambda} \frac{1}{2} \frac{eV(x,y,z)}{E} = \frac{\pi eV(x,y,z)dz}{\lambda E} = \sigma V(x,y,z)dz \quad (1.14) \]

where \( \sigma = \frac{\pi e}{\lambda E} \) is the interaction constant.

So the total phase shift can be given by

\[ d\phi \simeq \sigma \int V(x,y,z)dz \quad (1.15) \]
When the specimen is thin, we can express the potential experienced by electron throughout the sample to be

$$V_t(x,y) = \int_{0}^{t} V(x,y,z)dz$$ \hspace{1cm} (1.16)

thus the phase shift is

$$d\phi \simeq \sigma V_t(x,y)$$ \hspace{1cm} (1.17)

and the existing wave is now

$$f(x,y) = \exp[-i\sigma V_t(x,y)]$$ \hspace{1cm} (1.18)

Here we have ignored the adsorption of the material, since we are considering thin specimen. This is known as phase-object approximation, and the image taken is called phase contrast image. If we further consider the specimen to be very thin so that $V_t(x,y) \ll 1$, then $f(x,y)$ becomes

$$f(x,y) = 1 - i\sigma V_t(x,y)$$ \hspace{1cm} (1.19)

This further approximation is weak-phase-object approximation, from which the detected existing wave function is considered to be the direct representation of the electron potential of the specimen, thus the electron microscope images can be used to derive the structure of the specimen.

**Contrast transfer function - from exit wave to image**

The exit wave would transfer the the objective lens and form diffraction pattern on the back focal plane below the specimen, and image is formed by the interference of the diffracted waves on the image plane below the back focal plane, which will be then magnified by intermediate lens and projector lens. Let’s define the point-spread function of the objective lens to be $h(r)$, and the wave function at the image plane to be $g(r)$. The image formation process is actually a bridge from exiting wave $f(r)$ to $g(r)$, i.e.

$$g(r) = \int f(r')h(r-r')dr' = f(r) \otimes h(r)$$ \hspace{1cm} (1.20)

from equation (1.19), we can get

$$g(x,y) = [1 - i\sigma V_t(x,y)] \otimes h(x,y)$$ \hspace{1cm} (1.21)

$$= 1 + \sigma V_t(x,y) \otimes \sin(x,y) - \sigma V_t(x,y) \otimes \cos(x,y)$$
where \( h(x, y) \) is split into imaginary part and real part, *i.e.* \( h(x, y) = \cos(x, y) + isin(x, y) \). The image on the image plane is then \( I = gg^* \), and can be written as

\[
I = 1 + 2\sigma V_t(x, y) \otimes \sin(x, y)
\]

(1.22)

since \( \sigma = \frac{\pi}{LE} \) is small and the \( \sigma^2 \) and higher order are neglected. From equation (1.22) we can see that only the imaginary part of \( h(x, y) \) contributes to the final image, thus the Fourier transform of it can be written as

\[
H(u) = 2A(u)E(u)\sin \chi(u)
\]

(1.23)

where \( A(u) \) is the aperture function taking the value of 1 if the scattered beam falls inside the aperture, and 0 otherwise. \( E(u) \) is the envelope function standing for the damping effect coming from an incoherence of the electron beam. \( \sin \chi(u) \) is related to the defocus value, the wavelength of the beam, and the spherical aberration constant \( C_s \):

\[
\chi(u) = \pi[\lambda \cdot \Delta f \cdot u + \frac{1}{2} C_s \cdot \lambda^3 \cdot u^2]
\]

(1.24)

Defining the Fourier transform of \( g(r) \), \( f(r) \), and \( h(r) \) to be \( G(u) \), \( F(u) \) and \( H(u) \) respectively, then we can get from convolution theorem:

\[
G(u) = H(u)F(u)
\]

(1.25)

Taking equation (1.23) into equation (1.25) and set \( A(u) \) to be 1 since we only consider the beam passing through the aperture:

\[
G(u) = 2E(u)\sin \chi(u)F(u)
\]

(1.26)

From this we can see that the phase and amplitude of the structure factor \( F(u) \) is changed by the lens function \( H(u) \) after passing through the objective lens, *i.e.* the phase contrast is changed by the lens. Remembering that only the imaginary part of it plays the role, this part is called Contrast transfer function (CTF). A typical contrast function is shown in Figure 1.10, from which we could see, for \( |u| < 1nm^{-1} \), which is typical for mesostructures, the envelope function can be set to be 1.

### 1.2.3 3D reconstruction from TEM images

The process of structure reconstruction is essentially the reverse procedure of image formation process. In order to reconstruct the electron potential map, we need to get the structure factors:

\[
F(h, k, l) = \int \rho(x, y, z)exp[-2\pi i(hx + ky + lz)]dx dy dz
\]

(1.27)
The image is the projection of the 3D electron potential map into 2D image plane with some alteration originating from the CTF. Let’s assign the projection direction to be $z$. In this case the $l$ in equation (1.27) is 0 from the crystallography knowledge. Thus (1.27) can be written as:

$$F(h,k,0) = \int_{x,y} (\int_{z} \rho(x,y,z)dz) \exp[-2\pi i(hx + ky)]dxdy \quad (1.28)$$

in which the $\int_{z} \rho(x,y,z)dz$ is the same as $V_t$ in equation (1.16), which has a linear relationship with the exit wave as can be seen from Equation (1.19). Thus, after eliminating the effect of CTF (equation (1.22)), we can get the structure factor $F(hkl)$ directly from the images and reconstruct the 3D potential map by Fourier transformation:

$$V(x,y,z) = \frac{h}{2\pi me} \sum_{hkl} F(hkl) \exp[-2\pi i(hx + ky + lz)] \quad (1.29)$$

The procedure of the reconstruction can be graphically described in Figure 1.11.

For reconstruction of the mesoporous structure, we need to consider inherent structural fluctuation of mesoporous silica, which can originate from 1) lattice fluctuation 2) basis fluctuation and 3) surface roughness. As a consequence, the reconstructed map is effectively an averaged potential map for the material and the reconstructed structure is substantially indistinguishable. The solution is given by a representative unit cell that reflects the averaged structure of the material. A constant level is assigned to the potential map for the channel surface (equi-potential surface) that serves as the boundary between wall and pore structures, i.e., $\rho(r) = c = constant$. Then the argument comes
Figure 1.11: A graphic description of the reconstruction procedure

to the determination of \( c \), whose structural result should give some representative character of the material been reconstructed. The character often refers to the pore volume of the material and is determined by the gas-adsorption-desorption experiment.

1.2.4 Sample preparation methods

A proper sample preparation is necessary to obtain high-quality result from electron microscope, and in some cases special sample preparation is needed for specific purpose. One common requirement is an observation of the cross section of the samples, this requires a way of preparation that maximally maintain the inner features of the samples when cutting it. Argon ion milling is largely applied in this case. The ions break the atomic bond when hitting the sample, removing one side of the cross section and leaving other side intact. This makes it advantageous compared to mechanical milling especially for multi-content samples such as organic-inorganic mixture, where the boundary between soft and hard material can be easily smeared by external forces. The preference of argon comes from its inert property and its low atomic number, which minimize the reaction and facilitate a lower voltage to focus the beam during milling; both are essential to minimize the damage to the material during milling. Depending on the kind of microscope, the way of using
argon ion beam differs: for SEM, a pristine and flat cross section is needed where the surface of the section can be clearly seen; for TEM, thin slice is desired so that electron can transmit the sample to reveal specific part’s structure information. Two kinds of instrument are designed for these two purposes respectively, Cross section Polisher and Ion slicer. Both Cross section polisher and Ion slicer utilize the argon ion beam, with difference on the way the sample is polished. For Cross section Polisher, a molybdenum plate is placed on top surface of the sample to protect it from ion beam, while the part protruding from the shielding plate is milled by the ion beam so that a flat cross section is obtained. For ion slicer a thin (∼10µm) molybdenum tape instead of plate is applied, and the beam is designed to mill from both sides in angles of normally 0.50 – 30, so that a wedge like thin area can be obtained when a hole is being polished in the sample. Graphic representation of the both cross section and Ion Slicer is shown in Fig. 1.12.

1.3 Quasicrystal and Aperiodic tiling

Since the first discovery of quasicrystal in 1984 [62], the horizon of crystallography is extended from 3D to high dimensional space. There has been an extensive development in this field, both in obtaining new quasicrystal materials and developing corresponding theories [65]. In 1987 the first thermodynamically stable quasicrystal was obtained [72] and now the stable quasicrystal can be obtained even in binary system [71] with the structure of it able to be studied in atomic details [68].
Driven by its high symmetry and quasicrystallinity, potential usages of quasicrystalline structure have also been explored, especially in photonic devices through the realization of a complete photonic bandgap induced via multiple scattering of light waves in virtually all directions [47; 49]. This potential usage has encouraged scientists to strive for quasicrystals in larger length scales than on atomic scale. Although not so ideal compared to their intermetallic counterparts, quasicrystalline structures have been successfully obtained by self-assembly process in several systems in meso-scale range (20 to 500 ångströms), such as dendritic liquid crystals [77], ABC-star polymers [32], colloids [22] and inorganic nanoparticles [69]. They have formed a so-called “soft-quasicrystal” as they are all soft materials on contrary to the intermetallic counterparts.

As a hard template of the soft micellar structures, there exist high possibility that quasicrystal can be formed in mesoporous silica. Observations have shown the indication of dodecagonal quasicrystalline structure in AMS-2 material, where square and equilateral triangles combine in a modulated manner [28]. However, based on the well-indexed X-ray diffraction (XRD) pattern, this modification is considered more as periodic displacement during the growth of \( Pm\bar{3}n \) structure, an intrinsic property of the kinetic growth process. Learnt from previous experimental reports, we focused our research on the interval condition between the structure of \( Pm\bar{3}n \) and \( P4_2/mnm \), and have recently obtained the first hard quasicrystal in mesoporous silica. The revealed mechanism from the experimental results paves a positive prospects for future large-length-scale quasicrystals [74].

1.3.1 A general introduction

The “quasi” of quasicrystal has two meanings: 1) it is not ordinary crystal because it has no translational periodic order, 2) it is not amorphous or disordered material. It is called “crystal” because it has well-defined, discrete point group symmetry, and can produce sharp diffraction points under X-ray or electron beams. However the symmetry is incompatible with ordinary crystal which can only have 2-, 3-, 4-, 6- fold symmetries, instead quasicrystals have symmetries that are forbidden by translational periodicity: five-, eight-, twelve-fold, etc.

There are modulated and composite crystals whose structure cannot be indexed by 3D periodic lattices either. However, we can recognize prominent reflections constructing a 3D periodic lattice from the diffraction pattern of modulated structure. This means that modulated crystal has an average structure with 3D periodicity but are weakly perturbed from it. If there are two or more sets of 3D sub-lattices with periods incommensurate to each other,
it is called composite crystal. The quasicrystal differs from modulated and composite crystals in that it has no prominent reflections forming 3D periodic sublattices but the diffraction pattern shows a non-crystallographic symmetry.

The argument of multiply-twinned particles (MTPs) came along with the first discovery of quasicrystal. In Pauling’s argument to Shechtman’s icosahedral quasicrystal, he proposed a twinning model where the icosahedra of $MnAl_{12}$ (a Mn at the centre of a icosahedron with each vertex being a Al atom) share faces to assemble into a larger dodecahedron [57]. The dodecahedra, in Pauling’s theory, arrange to form the multiply-twinned particles that were supposed to explain the results obtained by Shechtman. Although such model was finally proved not matching the experimental data, it does not exclude the existence of the MTP. MTP particles were discovered in the gold, for example, where twenty patches of the FCC arranged gold atoms twinned together to form a icosahedron morphology, in an attempt to minimize the surface energy [37]. Such morphology has 5-fold symmetry but the inner periodic structure can be easily verified by TEM or XRD. In mesoporous silica, MTPs composed of twinned $Fm\bar{3}m$ structure were also obtained [50, 70]. Such multiply-twinned crystals are quite similar to the icosahedral gold particles, in terms of both structure and stabilization mechanism. These MTPs, although are not quasicrystal, have given a lesson of growth mechanism concerning surface energy aspect.

1.3.2 Aperiodic tiling

Some quasicrystals are considered to be 2D quasiperiodic, i.e. they are periodic in the third dimension. These quasicrystals are normally represented by an aperiodic 2D tiling. In addition to that, the 2D projections of the 3D quasicrystal in some specific directions reflect the essential information about the structure and thus a proper construction of the aperiodic tiling is important to serve as a structural model for real quasicrystals.

**High dimensional space**

Unlike the periodic tiling where two basic lattice vectors are enough for describing every vertices in the plane, higher dimensional space is needed to construct a 2D quasiperiodic tiling. To understand this, we can consider the Fibonacci chain, which is a 1D example of quasicrystal. The chain is composed of two kinds of segments: S and L (Short and Long), in a quasiperiodic sequence. Thus although the chain itself is 1D, there is no 1D unit cell that can be periodically repeated to give the quasiperiodic sequence of the chain elements. A 2D space is needed, as can be seen in Fig. [1.14] and the following discussion, to construct such quasiperiodic chain composed of two elements.
Figure 1.13: (a) The Penrose tiling with its four independent unit vectors to describe it. (b) The four pentagons of the occupation domain of the Penrose tiling, with each pentagon’s centre location marked. The colour of each pentagon corresponds to the subclass of vertices in the Penrose tiling.

This criteria can be simply extended to 2D tilings: the dimension needed is equal to the number of independent integer parameters needed to describe the tiling. Let’s now take another familiar example: Penrose tiling, a 5-fold quasiperiodic tiling. The tiling is constructed by two kinds of rhombi: the fatter one with acute angle $\frac{2}{5}\pi$ and the thinner one with acute angle $\frac{1}{5}\pi$. To describe the vertices inside the tiling, 4 independent unit vectors are needed, since 4 of the 5 kinds of rhombus edges are independent with respect to integer indices. Thus 4D space is needed to construct such tiling. The 4 basis vectors are however defined other than the edges of the rhombi, as shown in Fig. 1.13 for reasons of the specific 4D lattice type of Penrose tiling [38]. The vertices in the tiling are actually composed of four subclasses, each of which is obtained by section using one out of four pentagons that form the occupation domain. The four pentagons are embedded in perpendicular space and located at $(n,n,n,n)/5, (n=1,2,3,4)$ away from the lattice points in 4D space $(i,j,k,l), (i,j,k,l \in Integer)$, thus using the four basic vectors, the index of the vertices in the tiling is classified into 4 types:

1) $(1,1,1,1)/5 + (i,j,k,l)$
2) $(2,2,2,2)/5 + (i,j,k,l)$
3) $(3,3,3,3)/5 + (i,j,k,l)$
4) $(4,4,4,4)/5 + (i,j,k,l)$

The classification of the vertices and their corresponding pentagons as occupation domains are depicted by different colours in Fig. 1.13 For a more de-
tailed generation procedure of Penrose tiling, Reference [38] is recommended to read.

"Window" of aperiodic tiling

Like the case of Penrose tiling described above, the atoms that are projected into the physical space are just parts of the 4D lattice. Their distribution in perpendicular space is constrained in a limited area. In the case of Penrose tiling, it’s the four pentagons in Fig. 1.13(b). This constrained area is called “window” or “occupation domain” depending on the tiling-generation method: projection method or section method.

Projection method considers objects in higher dimension as points of 0 dimension while section method considers the “atoms” in higher dimension to have some shape in the dimensions perpendicular to the section plane. This can be understood by the example of Fibonacci chain. The projection of the 2 dimensional periodic lattice points on to the line with slope equal $1/\tau$ ($\tau = \frac{1+\sqrt{5}}{2}$) will produce a quasiperiodic sequence of distances between two adjacent points. The sequence can be described as LSLSLLSLLS... with L representing the larger distance between two adjacent points while S the smaller distance. The projection method in Fig. 1.14(a) has a strip (with width $\frac{1+\tau}{\sqrt{1+\tau^2}}$) parallel to the slope line for projection. Points within the stripe are projected onto the slope line and the projection can form a series of points with the arrangement of their adjacent distances corresponding to the Fibonacci sequence. The section method, on the other hand, extends each lattice point in the direction perpendicular to the slope line, into a line segment of length equal to the width of the strip in projection method (i.e. $\frac{1+\tau}{\sqrt{1+\tau^2}}$). In this case, the slope line is considered as a 1D section of the 2D space and the crossing points on it form the same Fibonacci sequence as in the projection method. The cross section of the stripe in the projection method is called “window” while the line segment on each lattice point in the section method is called “occupation domain”. These two methods are inherently the same in this case, just in different approaches. However the section method is more practically useful as it allows the occupation domain to locate diversely in the dimension of physical space. Like the case of Penrose tiling, the “atom” is composed of five pentagons separated from each other not only in perpendicular space, but also in physical space. The projection method can only project the 4D lattice to a window in perpendicular space and is insufficient to describe the locations of the occupation domain in the dimension of physical space. However the projection method is conceptually simple since it involves only point-like atoms.
Approximants and phason strain

Quasicrystal approximants exhibit full 3D translational periodicity, which is different from quasicrystal. However they are similar to quasicrystal in that their atom arrangements within unit cells are similar to the local atomic structures in quasicrystals. Moreover, the diffraction patterns of approximants are similar to quasicrystal but with lower symmetry. Considering high dimensional space, in the paragraphs above we described quasicrystal as the section through the physical space of the high-dimensional “atoms”, where the section plane is flat. If the section plane is bended in some manner or lies in directions nonparallel to the physical space, the section could result in some periodic approximants. How far away the bended or tilted plane is from the section plane in physical space can be expressed by a parameter called *Phason strain*, which
represents the closeness to the ideal quasicrystallinity.

There are two kinds of phason strains: linear phason strain and random phason strain. The concept of these phason strains can be understood by using the example of Fibonacci chain. This chain can be achieved by a section in 2D space. The section line, as can be seen in Fig. 1.14, is straight and in some specific direction so that the section points form a quasiperiodic sequence of Larger and Smaller intervals. If the section line is tilted into some other direction, the section points can become periodic, like the example in Fig. 1.15(a). In this case, since the section line is straight, \textit{i.e.}, linear, the only difference with that of quasiperiodic sequence is the tilting angle, and the phason strain is called \textit{linear phason strain}. There are also other cases where the section line is not straight, but randomly curved. Even though the average direction of the curve is in the direction of physical space, the random curves change the crossing places of the atoms and can introduce some randomness to the sequence of points projected onto the physical space. One example is give in Fig. 1.15(b), and the phason strain in such cases is called \textit{random phason strain}. Sometimes these two kinds of phason strains can coexist and there can be different ways of tilting and curving the section plane. If in some circumstance the outcome in the physical space is periodic, it is called \textit{approximant} to the quasiperiodic pattern. The less distorted the approximant’s section plane is compared to the section plan of quasiperiodic structure, the closer the approximant is to the real quasiperiodic pattern.

We can quantitatively specify the magnitude of linear phason strain if we know the physical vectors $\mathbf{r}^\parallel$ of the approximants’ coordinates and the corresponding perpendicular complement $\mathbf{r}^\perp$. If we assume the section surface is

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.15.png}
\caption{The graphic explanation of (a) linear phason strain and (b) random phason strain in the 1D example of Fibonacci chain. In (a) the scope angle is $\pi/4$ so that the chain obtained is periodic.}
\end{figure}

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sufficiently flat, then on average $r^\perp$ depends linearly on $r^{||}$, so that

$$r^\perp \cong Ar^{||} + \text{const}$$

(1.30)

where $A$ is called the phason strain tensor, and can be approached by a least-square fitting of a number of coordinates. As we know for a quasiperiodic pattern, the coordinates are restrained in a window in perpendicular space, so that $r^\perp$ is limited to some range, while $r^{||}$ can be infinitely expanded, thus $A$ is 0 for quasicrytalline tilings. For a linear case as in Fig. 1.15(a), $r^\perp$ increases linearly as $r^{||}$, thus $A$ is a non-zero tensor. For a random phason strain like Fig. 1.15(b), $A$ can be zero from least square fitting, however the deviation of $A$ is bigger than that of quasiperiodic pattern, as also can be verified by a larger projected area in perpendicular space.
2. Dodecagonal tiling in mesoporous silica

2.1 Background

Recent advances in the fabrication of quasicrystals (QCs) in soft matter systems have raised the length scales for QCs [62] into the meso range (20 to 500 ångström). So far, dendritic liquid crystals [77], ABC-star polymers [32], colloids [22], and inorganic nanoparticles [69] have been reported to yield QCs. These QCs offer larger length scales than intermetallic QCs (few Å’s), thus potentially leading to optical applications through the realization of a complete photonic band-gap induced via multiple scattering of light waves in virtually all directions [12, 47, 49]. However, the materials remain far from structurally ideal in contrast to their intermetallic counterparts, and fine control over the structure through a self-organization process has yet to be attained. Moreover, the soft-matter characteristic of these quasicrystals may limit their application, a hard-matter quasicrystal with large length scale is thus desired.

In the AMS system, two of the commonly observed crystal structures with the space groups $Pm\bar{3}n$ and $P4_2/mnm$ can be fabricated by merely varying alkalinity in synthesis [26]. These two structures are of particular interest in connection with dodecagonal quasicrystals (QCs) as they serve as approximants to it. In dendritic liquid crystal system dodecagonal QCs have been obtained under synthesis conditions between those for the two structures [77], it seems likely that QCs could also be synthesized between these two structures in AMS system.

We thus explore this anionic surfactant system by varying condition in the synthesis. It is found that an intermediate alkalinity leads to a crystal structure with the space group $Cmmm$. This new structure, however, is not the sole outcome of the synthesis. A structural study in the 12-fold cross section reveals an analogue of dodecagonal QCs in the center surrounded by twelve fans of crystalline domains in the peripheral part. The latter domains are composed of mainly $Cmmm$ structure. The quasicrystalinity has been verified by selected area diffraction and quantitative phason strain analyses on transmission electron microscope images obtained from the central region. We argue that the structure forms through a non-equilibrium growth process, wherein the com-
petition between different micellar configurations plays a central role in tuning 
the structure. A simple theoretical model successfully reproduces the observed 
features and thus establishes a link between the formation process and the re-
sulting structure.

2.2 Dodecagonal tiling

In order to study the dodecagonal quasicrystals, a proper model tiling is needed 
to describe the structure or use it as an reference of the experimental data. 
Considering the examples up to now, the dodecagonal square-triangle tiling is 
the most proper tiling to be compared with the experimental result. Based on 
this kind of model tiling, the “defects” can be defined and the experimental 
result can be quantitatively studied.

2.2.1 Tiling construction

As described in the Introduction chapter, the section and projection methods 
are mostly used to construct a 2D tiling from high dimensional space. The 
dimension needed is dependent on the tiling configuration. For a dodecago-
nal tiling where square and triangles are the main components, each edge is 
pointing to one of the 12 directions 30 degrees apart from each other. Thus 
we could assign 12 unit vectors for describing each vertices in the tiling, in 
which only 4 of them are linearly independent with each other with respect 
to integer index numbers. In this case the 4 dimensional space is required at 
least for constructing the dodecagonal tiling. Let us define the unit vectors 
in physical space to be: $e_j = \cos(\pi j/6), \sin(\pi j/6)$ with $j = 1 - 4$. Thus each 
vertex in the tiling can be described by $r = n_1 e_1 + n_2 e_2 + n_3 e_3 + n_4 e_4$, where $n_j$ 
($j = 1 - 4$) are integers that correspond to the lattice in 4D space. A definition 
of the perpendicular space unit vectors and proper choice of the occupation 
domain could result in a dodecagonal quasiperiodic tiling. Any shape can be 
chosen to be the occupation domain as long as it preserve the symmetry of the 
4D lattice in the physical space (12 fold symmetric in the case of dodecagonal 
tiling). If a simple dodecagon is used as occupation domain, the 12-fold sym-
metrical quasiperiodic tiling can be obtained in the tiling. However the tiling 
contains not only squares and equilateral triangles, but also trigonal hexagons 
or rhombuses depending on the size of the occupation domains (Fig. 2.1). 
These two additional tiling units are also occasionally found in the real ma-
terials [32, 39, 69], but not so densely distributed as the tiling obtained by 
simple dodecagon (actually they are more considered as “defects” instead of 
tiling components). Other forms of 12-fold polyhedrons as occupation domain 
cannot get dodecagonal tilings composed of only squares and triangles either.
Figure 2.1: The tilings obtained by simple dodecagon window with different window sizes, in (a) the smaller window (distance from dodecagon center to vertices 1.01) produces mainly trigonal hexagons in addition to squares and triangles while a larger window (distance from dodecagon center to vertices 1.1) in (b) fill the hexagons in (a) with rhombuses, squares and triangles.

One kind of occupation domain that can produce dodecagonal square-triangle tiling is a fractal, in which an affine similarity transformation is performed to iteratively generate an unconnected occupation domain (Fig. 2.2) [5]. One possible disadvantage of this kind of iterative loop is that it can be as long as infinity and thus would consume large computing energy for large tilings.

There are other methods that can be employed to try to give an satisfactory
Figure 2.2: The dodecagonal quasiperiodic square-triangle tiling obtained by the fractal window \[5\].

result. One of them is the inflation method where the self-similarity property of dodecagonal quasiperiodic tiling is employed \[33, 64, 76\]. This method is intuitive as it’s handled merely in physical space: starting from a square-triangle tiling patch, each square and triangle is inflated according to the inflation rule and generate a larger tiling. With this process running iteratively, the tiling is closer and closer to a quasiperiodic square-triangle tiling. Although practically satisfactory for modelling real systems, this method actually generate approximants unless the inflation goes to infinity. Recently an method of point process is invented to generate the decagonal quasiperiodic tilings. Like inflation method, the process is only in physical space and can be automated with a finite number of rules. This method has generated a series of new decagonal quasiperiodic tilings with chiral occupation domains showing fractal boundaries \[24\]. Although no direct example is presented up to now, the method is promising in generating dodecagonal square-triangle tilings.

2.2.2 Topological defects

Each vertex in the square-triangle tiling can be uniquely defined by the 4 unit vectors, and thus corresponds to one unique point in the 4D lattice. The 4D coordinates can also be uniquely determined from the tiling containing trigonal hexagons and rhombuses, or in general, from tilings obtained by idealized mathematical formulas. However, in real materials, the edges of the tiling are not precisely oriented to the unit vectors, and are connected with the 4 unit vectors with some endurance, and defects of other kinds may exist in such tilings. Some of these defects give non-zero value when adding their edges that make
a closure, and are called topological defects (Fig. 2.3). To represent the tilings with topological defects, modification of the lattice points in the 4D space is needed, in order that the projection of the 4D points into physical space can match with the real tilings. For this reason, each topological defect needs a characterization by Burgers vector:

$$\mathbf{b} = \sum_j \mathbf{e}_j = [b_1 b_2 b_3 b_4]$$ (2.1)

i.e., the sum of the (idealized) vectors $\mathbf{e}_j$ tracing the edges of the associated polygon counter-clock-wise. If a close trajectory goes around a topological defects counter-clock-wise, the indices will change by $[b_1 b_2 b_3 b_4]$ after every round. Hence, the indices $[n_1 n_2 n_3 n_4]$ for any vertex are indefinite through an addition of the extra amount. In order to remove this arbitrariness, one can constrain the process to determine the indices in such a way that $[b_1 b_2 b_3 b_4]$ is subtracted when we cross the $\theta = 0$ line ($\theta$: azimuthal angle for the 2D polar coordinate system taking the defect center as the origin) from the topological defect. Indexing can be fixed in this manner for any number of topological defects. However if we project such indexed 4D lattice into physical space, one can find that the projection does not match with the original tiling, some close-distance points or tears would appear in the projection. As a remedy for this mismatching of the model tiling, the points in 4D space need to be shifted from their ideal lattice sites, so that:

**Figure 2.3**: Two defects in the square-triangle tiling, the close trajectory of the trigonal hexagon defect gives 0 thus is not a topological defect while that of the pentagonal defect gives a non-zero $[-1, 0, 2, -2]$ and is a topological defect with the Burgers vector $[-1, 0, 2, -2]$
\[ r' = r - \sum_k \frac{\theta(r' - c_k)}{2\pi} b_k \]
\[ r'^\perp = r'^\perp - \sum_k \frac{\theta(r' - c_k)}{2\pi} b_k'^\perp \] (2.2)

where \( c_k \) denotes the center position of the \( k \)-th topological defect and \( \theta(r) \) is the azimuth of the vector \( r \) \[44\]. (The corrected coordinates \( r' \) are also involved in the right hand sides to determine the azimuth angles, implying these equation have to be solved self-consistently for \( r' \). For convenience, however, the azimuth angles in the right hand sides can normally be safely replaced with the ones obtained from “observed” coordinates, since the associated errors are negligibly small.) Based on this corrected vectors, the calculated phason strain tensor is truly that of the observed tiling.

2.2.3 Approximants and polyhedron model

There are four common approximants that are closely related to the dodecagonal square-triangle tiling: \( 4^4 \), \( 3^6 \), \( 3^3.4.2 \) and \( 3^2.4.3.4 \). They belong to the 11 Archimedean tilings, which allow only one kind of vertex in each tiling (Fig. 2.4). These tilings are named after the vertex of the tiling by a set of integers.

\[ \text{Figure 2.4: The 11 Archimedean tilings} \]
“\(n_1, n_2, n_3, \ldots\)”, meaning that surrounding each vertex the polygons \(n_1\)-gon, \(n_2\)-gon, \(n_3\)-gon, \ldots tile in a cyclic manner. Superscripts are used as a degeneracy of two identical polygons that are adjacent. The four approximants are composed of purely squares and/or equilateral triangles and their phason strain tensor can be calculated from equation (1.30) to be \(\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\), \(\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}\), \(\begin{pmatrix} -0.134 & -0.232 \\ -0.232 & 0.134 \end{pmatrix}\) and \(\begin{pmatrix} -0.134 & -0.232 \\ -0.232 & 0.134 \end{pmatrix}\) for \(4\), \(3.6\), \(3.4^2\) and \(3.2.4.3.4\) respectively. One can also use analytical method instead of least square fitting to calculate the phason strain tensor for these approximant tilings, since they are periodic in 2D, meaning their coordinates are linearly arranged in 4D lattice, \(i.e.\) they have purely linear phason strain.

One thing that needs notification is that once the unit vectors are chosen differently, or the tiling is rotated some 30 degrees, the phason strain tensor gives a different form. This makes the phason strain comparison between tilings difficult. Thus the phason strain tensor is expressed as

\[
A = \begin{pmatrix} \alpha + \gamma & -\beta + \mu \\ \beta + \mu & \alpha - \gamma \end{pmatrix}
\]

(2.3)

where \(|\alpha|, |\beta|\) and \((\gamma^2 + \mu^2)^{1/2}\) are invariant under rotation of \(2\pi n/12\). They can be used as the representation of the magnitude of the phason strain \([44, 54]\). Another parameter \(\lambda\) is also often used as a measure of the strength of the linear phason strain, which is the square root of the major eigenvalue of the symmetric matrix \(A^T A\) \([53]\). For a rough estimation of the phason strain tensor, one can calculate the number ratio of squares and triangles in the tiling. For a dodecagonal quasiperiodic tiling, the ratio of the number of triangles to that of squares equals \(4/\sqrt{3} \approx 2.31\) \([44]\). From this aspect the \(3.6\) and \(4\) tilings are likely to have larger phason strain than \(3.2.4.3.4\) and \(3.4^2\), which have twice as many triangles as squares.

In mesoporous materials three of the structures can correspond to the approximant Archimedean tilings. Their space groups are \(Pm\bar{3}n\), \(P4_2/mnm\), and \(Cmmm\). When viewed from their [001] directions, their projected images form the tiling of \(4\), \(3.2.4.3.4\) and \(3.4^2\) respectively (Fig. 2.5). These structures are know as tetrahedrally close-packed structures \([9]\) of micelles (Fig. 2.6) encaged by silica, which remains in the final material representing the Voronoi tessellation for the micellar packing \([46]\). A similarity of these structures can be found in foams \([46]\) and their cage type pores can be conveniently described by polyhedron models if each cage-type pore is analogized to a polyhedron, with the polyhedron faces representing the collecting pore openings \([58]\). In this manner, the \(Pm\bar{3}n\) structure, whose lattice corresponds to the A15 type structure of alloys \([8]\), can be described by two kinds of Voronoi polyhedra,
Figure 2.5: The TEM images in [001] direction of (a) $Pm\bar{3}n$, (b) $Cmmm$ and (c) $P4_2/mnm$ structures. The yellow and white lines in each TEM image show the corresponding tiling and the orthogonal unit cell. The corresponding 3D micellar coordination models are shown on the right part respectively, with each sphere representing one micelles. The colours of the sphere depict the micelles of different kind, which can be further demonstrated by polyhedron models (Fig. 2.6).
[5^{12}6^2] and [5^{12}], where the [5^{12}] polyhedra serve as the connection between columns of stacked [5^{12}6^2] polyhedra along the [001] direction. On the other hand, the $P4_2/mnm$ and $Cmmm$ structures, whose counterparts in alloys are the $\sigma$ [7] and $H$ phases [34], respectively, require an additional kind of polyhedra, [5^{12}6^3], to fill in the space among triangularly arranged [5^{12}6^2] columns.

![Figure 2.6:](a)The polyhedron models of the cage-type materials that give projection of squares and triangles. The three kinds of Voronoi polyhedra \([5^{12}6^2]\), \([5^{12}6^3]\) and \([5^{12}]\) are shown blue, red and yellow, respectively. (b) Projections of the polydehedral frames, demonstrating the 2D-3D relationship of the squares and triangles.

2.2.4 The structure factor of dodecagonal quasiperiodic tiling

As the dodecagonal quasiperiodic tiling is constructed by “atoms” in the 4D space, it would be natural to think of the structure factor to be calculated by Fourier transformation in 4D space. In the case of section method, as the occupation domain is in the perpendicular space, from the property of the Fourier transformation, the diffraction pattern of the section of a structure is given by the projection of the structure factor along the complementary space, i.e. normal to the external space. This property in principle interprets the diffraction pattern of the quasicrystalline structures and supports the high dimensional space description of the quasicrystals.

The structure factor can thus be calculated from a theoretical model in high dimensional space by Frouier integral of the electron density in a unit cell of \(nD\) space. Just like that for 3D periodic crystals, the high dimensional structure is a convolution of the occupation domain and the 4D lattice coordinates, and the calculation can be reduced to the Fourier integral of the occupation domain and the phase factor related to the location of the domain. To give an analytical expression of the integral for a complicated occupation domain is not an easy
task, but is possible for domains composed of polygons or even circles in a 2D internal space, and it adopts the form [75]:

\[ F(h) = \sum_{\mu} \sum_{\{R|t\}^\mu} f^\mu(h^\nu)p^\mu \exp[-B^\mu(h^\nu)^2/4] \times \exp[2\pi i h \cdot (R^\mu + t)]F_0^\mu(R^{-1}h) \]

(2.4)

where \(r^\mu, B^\mu\) and \(p^\mu\) are the position, temperature factor and occupancy of the \(\mu\)th independent occupation domain, and \(F_0^\mu\) and \(f^\mu(h^\nu)\) are the Fourier integral and atomic scattering factor of the \(\mu\)th occupation domain. The sum of \(\{R|t\}\) runs over the symmetry operators that create the symmetrically related occupation domains inside the same unit cell as the independent occupation domains.

A simpler form can be obtained if the occupation domain is a circle with radius \(r\), and the temperature factor and occupancy factor are assumed to be unity, the Fourier integral takes the form:

\[ F_0^\mu(h) = 2VJ_1(q_0)/q_0 \]

(2.5)

with \(V = \pi r^2\) and \(q_0 = 2\pi h/r\), where \(J_1\) is the Bessel function of the first order. Based on this function, a diffraction pattern of the dodecagonal tiling can be calculated and is shown in Fig. 2.7.

Figure 2.7: (a) The simulated diffraction pattern of (b) the dodecagonal quasiperiodic tiling obtained by a circular occupation domain of radius 1.05
2.3 Synthesis of the material

A series of synthesis trials were carried out in close proximity to where the $Pm\bar{3}n$ and $P4_2/mnm$ structures have been reported in the $C_{14}$GluA/NaOH/TMAPS triangle synthesis-field diagram [26] (Fig. 2.8). The TMAPS/$C_{14}$GluA molar ratio was kept constant at 1.1, while the NaOH/$C_{14}$GluA molar ratio was increased step-wise from 1.0 to 1.8 with an interval of 0.1. The $P4_2/mnm$ structure was dominant when the NaOH/$C_{14}$GluA molar ratio was 1.8, while at 1.7 dodecagonal-shaped particles with the Cmmm structure became the majority, and finally the $Pm\bar{3}n$ structure was obtained at 1.3. The sample from which Fig. 2.12(b) was taken was obtained in another synthesis trial, which was carried out at a molar ratio of $C_{14}$GluA/TMAPS/NaOH = 1:1.5:1.5, where structure with a space group $Fd\bar{3}m$ was previously reported. The synthesis conditions of $Fd\bar{3}m$ and $Pm\bar{3}n$ can be quite close to each other and a mixture of them is quite often obtained in one sample patch. We expect this particular particle in Fig. 2.12(b) to be an derivative of $Pm\bar{3}n$ or $P4_2/mnm$ instead of $Fd\bar{3}m$ since the polyhedron model of $Fd\bar{3}m$ is quite different from that of $Pm\bar{3}n$ and $P4_2/mnm$ [58], and can hardly be related to the square-triangle tiling. The following conditions were kept constant throughout all the syntheses: concentration of the surfactant in water=1 wt%; TEOS/surfactant=15; synthesis temperature= 70°C.

A typical synthesis of mesoporous silica, as exemplified by the case of obtaining the dodecagonal particles, proceeds as follows: $C_{14}$GluA (0.357 g, 1 mmol) was first dispersed in deionized water at 70°C. To the solution, 0.5M NaOH (3.42 g) was added with stirring. A mixture of TEOS (3.12 g, 15 mmol) and TMAPS (0.571 g, 1.1 mmol, 50 wt% in methanol) was added with stirring.
After ten minutes the stirring was stopped and the reaction mixture was aged at 70°C for two days. The precipitate was filtered, dried at 60°C, and calcined at 550°C for six hours to give surfactant-free mesoporous silica.

2.4 Structural characterization

2.4.1 XRD characterization

The XRD patterns of the synthesis patches have shown that the structure evolves from 2D hexagonal to $Pm\bar{3}n$ with increasing amount of NaOH (Fig. 2.9). This is in accord with the fact that higher ionization degree of the head group increases the repulsive force between head groups, leading to a higher curvature of the surfactant micelles, which templates to mesoporous structures with higher surface curvature, i.e. from columnar to cage type [26]. Above a certain molar ratio of NaOH/C$_{14}$GluA the XRD pattern is hard to interpret as peaks are broaden. This happens quite often to mesoporous silica materials, as the soft-matter character of the surfactant template may cause the lattice and basis fluctuation of the porous structures, or several structures coexist in the same sample patch, both cases lead to the broadness of the peaks in XRD pattern as it is a characteristic of a massive sample particles. The distinct peaks, though broaden, still point to the existence of crystalline structure, however the detail needs characterization in finer scale, and electron microscopy comes in to play in this role.

2.4.2 Morphological study by SEM

SEM observation can distinguish some particles with known space group [26], derived from the point group symmetry of the particle morphologies. Some morphologies correspond well with the XRD patterns like that of $Pm\bar{3}n$ space group, whose cube-like morphologies correspond to the $m\bar{3}m$ point group symmetry (Fig. 2.10(a)). The particles with $P4_2/mnm$ space group is also able to be picked up by the $4mm$ point group symmetry of their morphologies (Fig. 2.10(b)). However not all particles give well-shaped morphology according to their structures, like the case of $P6mm$. The worm-like morphologies do not show any six-fold symmetry (Fig. 2.10(c)), although their XRD pattern says clearly their space group. There are also quite many particles with no well-defined shapes probably due to fast condensation of the silica species during particle growth, or are impurities caused by the hydrolysis and condensation of silica oligomers without being templated by surfactant micelles. Judgement is thus done only from those well-shaped particles if the space group cannot be derived from just XRD pattern.
Figure 2.9: The XRD patterns of the synthesized materials (X-ray wavelength 0.154nm). All the samples were synthesized keeping the TMAPS/$C_{14}$GluA molar ratio constant at 1.1, while from the bottom to the top of the graph the NaOH/$C_{14}$GluA molar ratio was increased step-wise from 1.0 to 1.8 with an interval of 0.1.

The SEM observation has found that the $P4_{2}/mmn$ is more dominant at higher NaOH ratio while $Pm\bar{3}n$ takes the majority at lower NaOH ratio for the samples with broaden XRD patterns (Fig. 2.9). Interestingly, between these synthesis conditions there is one more prevailing morphology that gives
Figure 2.10: The typical morphologies of particles with space group of (a) \( Pm\bar{3}n \) and (b) \( P4_2/mnm \) together with (c) the worm-like morphology of the particles whose XRD pattern give the space group of \( P6mm \)

Figure 2.11: The SEM image of the samples with morphology of dodecagonal prism

a “forbidden” point group symmetry: 12-fold (Fig. 2.11). The dodecagonal prism morphology cannot be attributed to any known space group as only 2-, 3-, 4-, or 6- fold symmetry is allowed in crystallography if the crystal has translational periodicity. Two probabilities can be thought of about this special crystal: a dodecagonal quasicrystal or a twinned structure (or a combination of both). How the inner structure is related to the structures of \( Pm\bar{3}n \) and \( P4_2/mnm \) would also be interesting to explore.

2.4.3 Tilings under TEM

To observe the samples in TEM, normally the mesoporous silica particles are crushed into tiny pieces so that some thin enough (less than 100nm thick) areas can be obtained when the particles break into pieces. Observation based on the crushed samples revealed that a mixture of structures exist (\( Pm\bar{3}n \), \( P4_2/mnm \),
Figure 2.12: Two examples of the crushed samples that have a 12-fold diffraction pattern indicating a possibility of dodecagonal quasicrystals, the image in (b) was taken from a sample with synthesis condition slightly different from the sample patch with dodecagonal prism morphology, but at the synthesis condition where $Fd\bar{3}m$ was reported to be synthesized [26].

$Cmmm$ or the modulated structures of these three) in the sample patch of dodecagonal prism morphology. None of these structures are likely to form the dodecagonal prism morphology by itself. Occasionally, some thin pieces show a diffraction pattern of 12-fold symmetry (Fig. 2.12), indicating the possible existence of dodecagonal quasicrystal. However the crushed pieces lost their location information relative to the crystal particle, thus the mixed structural result could not give a direct description of the structure of the whole particle. Ion slicer is applied in this case to make thin slices of whole particles so that a characterization of the tiling distribution inside the crystal is possible.

The slices show a randomly tiled center surrounded by twelve fans composed of more periodic tilings in the peripheral region (Fig. 2.13). Each fan is a combination of rows of squares and equilateral triangles parallel to the edge of the dodecagon, forming $3^3\cdot4^2$ and $4^4$ vertices. Between two adjacent fans that differ by 30 degrees in orientation there is a common narrow boundary area with $3^2\cdot4\cdot3\cdot4$ vertices, defects, and/or dislocated rows of squares and triangles (Fig. 2.14(c)). The defects adopt different configurations and some frequently observed ones in the boundary part are shown in Fig. 2.14(d). Inside a fan defect may also exist. A smaller fan-like arrangement may also grow from this defect, and can be incorporated into a major fan on either side. Hence, a fan may consist of several parallel domains bounded by defect rows (Fig. 2.14(b)). Although the arrangement can be seen as a 2D analogue of a multiply-twinned
A graphical description of the tiling distribution concluded from TEM observations on various sample slices: A randomly tiled center surrounded by twelve fans of more periodic tilings.

A qualitative proof of the tiling distribution can also be made through diffraction experiments. A diffraction taken from the center of an ion sliced sample along the dodecagonal axis is shown in Fig. 2.16(a). The pattern nicely compares with a simulated pattern with a dodecagonal quasiperiodic tiling. On the other hand, if the contributions from peripheral fans are included, some of the noticeable peaks fail to be indexed by a dodecagonal quasiperiodic tiling, and also many diffuse scattering features due to twinning are observed. An extra peak indicated in Fig. 2.16(b) is associated with the 400 reflection for the Cnmnn structure; the intensity of this peak as well as that of other diffuse features is reduced significantly when the aperture is narrowed. This diffraction result supports the tiling distribution map depicted in Fig. 2.13.
Figure 2.14: (a) Low-magnification TEM image indicating the in-fan part and the boundary part, where high-mag TEM images are taken in (b) and (c) respectively. A larger view of the location of each part is also put in the right bottom of each image in (b) and (c). In (b) two parallel domains constituting a single fan separated from each other by a defect row (yellow). Within each domain, linear rows of vertices are marked with dotted lines with the colours: pink, 3\(^3\), 4\(^2\) vertices; light blue, 4\(^4\) vertices. In (c) irregular polygons (yellow lines) are observed in the boundary area between two fans. Linear rows of vertices within each fan are marked with broken lines with the same colour language same as in (b). A defect row bounding two parallel domains is marked by white lines. Defects that are frequently observed between fans are displayed in (d).

2.5 Phason strain analysis of the tilings

The tiling extracted from the TEM images are taken to be the 2D physical space of the 4D hyper space. Each vertex in the tiling is connected to any of its adjacent vertices by one of the linearly independent unit vectors \( \mathbf{e}_j = (\cos(\pi j/6), \sin(\pi j/6)) \) with \( j = 1 \sim 4 \). In this way each vertex in the tiling is
Figure 2.15: Main panel, a TEM image taken from the central part of a sample (as indicated in the top left inset), where the tiling edges are superposed on the image. The colours of the edges correspond to the six unit vectors in physical space as shown in the bottom left inset. FFT of the main-panel image is shown at the top right inset.

represented by the vector:

\[ r = \sum_{j=1}^{4} n_j e_j \]  

(2.6)

where the integer coefficients \( n_j \) are the indices of the 4D lattice. The coordinates can thus be lifted into a 4D hyperspace via \( \rho = (r, r^\perp) \), where the perpendicular components are defined by

\[ r^\perp = \sum_{i=1}^{4} (-1)^i n_i e_i \]  

(2.7)

where \( e_i \) are the same unit vectors as in Equation (2.6). By definition, \( \rho \) belongs to a periodic lattice called the dodecagonal lattice in 4D space generated by the 4D basis \( \tilde{e}_j = (e_j, (-1)^j e_j) (j = 1 \sim 4) \).

The vector \( r \) in the physical space as well as \( r^\perp \) in the perpendicular space is an orthogonal projection of the vector \( \rho \) in 4D space onto the respective subspace. There is a bijection (i.e., one-to-one correspondence) \( r \leftrightarrow r^\perp \) between the coordinates in the two subspaces since each vector is uniquely determined by the indices \([n_1n_2n_3n_4]\). The vertices of a tiling in physical space
can thus be mapped into perpendicular space, leading to a distribution of points called the “conjugate image” of the tiling. The linear phason strain tensor \( \mathbf{A} \) can be evaluated via a linear least-squares fitting, which minimizes the sum \( v = (1/N) \sum |r^- - \mathbf{A}r - t_0|^2 \) over the vertices contained in the tiling (\( N \) is the number of vertices).

Considering the topological defects in the tiling, the indexing is performed under some constraint, \textit{i.e.} if a closed trajectory goes around a topological defect counter-clock-wise, the indices will change by the Burgers vector \([b_1b_2b_3b_4]\) after every lap. For convenience, one can also constrain the indexing so that no closed trajectory around the topological defect is made. An example is demonstrated with the tiling in Fig. 2.12(a) (Fig. 2.17). A remedy using Equation (2.2) can then be utilized to correct the lattice shift due to the topological defects.

For the tiling in Fig. 2.15, the conjugate image is much more scattered than the “window” of a square-triangle DQT (Fig. 2.18), indicating a significance of the “phasonic disorders” in the structure, although the phason strain tensor is evaluated to be small. A measure on the root mean square of the deviation \( |r^- \mathbf{A}t_0| \), \textit{i.e.}, \( d = \sqrt{v} \) gives value significantly larger than the unity.
Figure 2.17: (a) the tiling extracted from the TEM image in Fig. 2.12(a), with the topological defect marked by a red dot. (b) the topological representation of the index process, where the colors of the edges represent the four unit vectors in physical space. The origin is randomly chosen and is marked by a Blue dot. The red dot gives the center of the topological defect and the index was done so that it does not cross over the horizontal dashed line originated from the red dot.

(Table 2.1), meaning a random phason disorder along the inclined direction of the section surface in 4D space (de Bruijn surface). A close inspection suggests that the tiling can be decomposed into several domains, each of which has some trend of periodicity. A few of the domains are composed purely of $3^34^2$ vertices. We may also extract three domains, shown by red and blue backgrounds in Fig. 2.18, which admit periodic continuations, i.e., they can be embedded in two kinds of approximants, Approximants 1 and 2, defined in Fig. 2.19. Note that Approximant 2 is an intermediate structure between $3^34^2$ and $3^24.3.4$, as it includes both these vertex classes while keeping the triangle/square ratio at two. Approximant 1 is somewhat different since it contains $3^6$ vertices. Selected properties of different tilings are summarized in Table 2.1, in which the values of $\lambda = \sqrt{\alpha^2 + \beta^2} + \sqrt{\gamma^2 + \mu^2}$, namely, the square root of the major eigenvalue of the symmetric matrix $A^TA$, are given as a measure of the strength of the linear phason strain.

The tilings have different configurations depending on individual samples. For instance, the tiling shown in Fig. 2.12(a) has a corresponding conjugate image less scattered than that in Fig. 2.15, and a least-squares fitting gives a smaller $d$ value than the variation of the phason shifts $Ar$ over the whole tiling. Still the linear phason strain is evaluated to be somewhat stronger than in Fig. 2.15 (Table 2.1). As in the case above, a sub-domain that admits a periodic continuation can be extracted. The yellow part in Fig. 2.18 can
Figure 2.18: Three tilings (from top to bottom) derived from Fig. 2.15, Fig. 2.12(a) and Fig. 2.12(b), respectively. The centers of the topological defects are indicated by black dots in the first and second tilings. In the respective right panels the conjugate images of the vertices in the perpendicular space are shown by dots (the topological defects have been remedied). The blue regions in the background show the size and the shape of the window for an ideal doddeagonal quasiperiodic tiling (Fig. 2.2). Four kinds of approximants are extracted from the tilings, and are indicated by color fillings: Approximant 1 (red), Approximant 2 (blue), Approximant 3 (yellow) and Approximant 4 (green). The numbers of triangles and squares in (a), (c) and (e) are (615, 263), (382, 170) and (323, 142), respectively.
be embedded in Approximant 3 (Fig. 2.19), whose linear phason strain is of the same strength as that for the Archimedean tiling $3^2.4.3.4$ (Table 2.1). The tiling in Fig. 2.12(b) is even closer to a dodecagonal quasiperiodic tiling (Fig. 2.18). No topological defects were observed in the illuminated area the relevant phason space parameters were evaluated by fixing the value of $\beta$ to be 0 because the tiling consists only of squares and triangles [40]. This is indeed the closest tiling to a dodecagonal quasiperiodic tiling among all the tilings obtained from our samples. Approximants 3 and 4 are extracted from the tiling as shown in Fig. 2.19.

**Figure 2.19:** The four Archimedean tilings composed of squares and triangles are aligned in the first row, while the four approximants extracted from the samples (Fig. 2.18) in the second row. From approximant 1 to approximant 4, the triangle/square number ratio are 2.57, 2, 2.2, 2.33 respectively.

All these tilings, with different configurations and various phason strain features, are similar in the sense that they are composed of randomly arranged approximants in different orders close to dodecagonal quasiperiodic tiling. The linear phason strains of the tilings are averaged from their constituents to give a smaller value. This common randomness feature strongly suggests a non-equilibrium formation process, a growth process that may lead to the so called random tiling quasicrystals [54].
\[
\alpha = \beta \left( \gamma^2 + \mu^2 \right)^{1/2} \lambda \ d
\]

Table 2.1: The phason strain parameters for the specific extracted from the sample as well as those for the whole samples are summarized. The values for the two Archimedean tilings, $3^3.4^2$ and $3^2.4.3.4$, and an ideal dodecagonal quasiperiodic tiling constructed by the unit dodecagonal window are also given for reference.

| Approximant | $|\alpha|$ | $|\beta|$ | $(\gamma^2 + \mu^2)^{1/2}$ | $\lambda$ | $d$ |
|-------------|-----------|-----------|----------------|--------|-----|
| 3^3.4^2     | 0.464     | 0.536     | 1              | 0.464  |
| Approximant 1 | 0.293     | 0.179     | 0.471          | 0.714  |
| Approximant 2 | 0.155     | 0.309     | 0.464          | 0.664  |
| 3^2.4.3.4    | 0.070     | 0.010     | 0.176          | 1.043  |
| tiling in Fig. 2.15 | 0.123 | 0.032 | 0.083 | 0.211 | 1.640 |
| tiling in Fig. 2.12(a) | 0.070 | 0.010 | 0.176 | 0.247 | 1.043 |
| Approximant 3 | 0.170     | 0.098     | 0.268          | 0.702  |
| tiling in Fig. 2.12(b) | 0.054 | 0.071 | 0.124 | 0.916 |
| Approximant 4 | 0.268     | 0.268     | 0.678          |
| Dodecagonal quasiperiodic tiling (dodecagon window) | 0.070 | 0.010 | 0.176 | 0.247 |

2.6 Growth simulation and growth mechanism

This part is mostly developed by Dr. Nobuhisa Fujita [74]. I introduce here the basic idea of the simulation and the correspondingly derived growth mechanism of the crystal for the integrity of the thesis. The simulation was hinted by the observation of the dodecagonal shaped particles whose quasicrystalline centre and a twin-like arrangement in the peripheral part strongly suggest a non-equilibrium formation process. The physical mechanism consideration was based on some previous theoretical analysis on the stability mechanism of the $Pm\bar{3}n$ structure, in terms of an area-minimization principle for the interfaces [15, 46, 56]. However these theories does not go beyond the periodic approximant structures. For simulating the non-periodic structural features of our material, a new approach is introduced. In this approach, the three-dimensional structures is abstracted as projected tilings in a plane. And an emphasis is put on the growth of the whole particle instead of the unit cell of a periodic structure. The choice of the growth size is done by a modified Monte-Carlo process that constrain the simulation results to be square-triangle tilings and meanwhile gives insight into the physical energetics that govern the final configurations of the tilings.

As the 2D projected image of our material is composed of mostly squares and triangles, we constrain the simulation so that a growing cluster at any
Figure 2.20: The graphic description of the modified Eden process used in our simulation. (a) A initial square-triangle tiling is used as the starting point, around one vertex in the tiling, twelve candidate-positions are marked by green dots (b) Candidate-positions are chosen for all the vertices on the surface of the initial tiling, with those points inside tiling removed. (c) One candidate site is occupied once it has been chosen \( m \) times, new candidates are generated around this new vertex to participate in the next round of choosing process, together with those favoured candidate-sites (chosen more than “\( m/2 \)” times in the first round, marked in blue) left from the previous round. (d) New site is occupied when it’s been chosen \( m \) times and the process continues like in (c).

Instant is represented as a patch of square-triangle tiling, and candidates for a new vertex are defined as all the positions that lie outside the patch and that are connected to any vertex on the outer boundary through one of the unit vectors \( e_j \), with \( j = 1 − 12 \). Enlightened by the Monte Carlo method, an occupation rate \( p \) is used for governing the growth of the tiling. For each candidate \( p \) is given by \( p = p_0 [1 - exp(\Delta E / T)] \) for \( \Delta E < 0 \) and \( p = 0 \) for \( \Delta E \geq 0 \), where \( \Delta E \) is the increment of total energy on occupying the candidate vertex, and \( p_0 \) (the sampling rate) and \( T \) (temperature) serve as proper scales for the probability. 
ity and energy, respectively. Growth proceeds by repeatedly making a random choice from the candidates with even probability, and by occupying a candidate vertex once it has been chosen a certain number of times, \( m \). The value of \( m \) is associated with \( p \) and in our case is given as an integer that approximates \( 1/p \), whereas any candidate with \( p = 0 \) is rejected. The larger scale we set the value of \( m \), the less noise the random choosing procedure can have in reflecting the energy-governing growth process. This stochastic model is a modification of the Eden process, which was originally introduced to analyse the non-equilibrium growth of a colony of cancer cells or bacteria. A graphic description of this process is demonstrated in Fig. 2.20.

2.6.1 Potential expressed by square-triangle configurations

The \( \Delta E \) plays the crucial role in defining the occupation rate and thus the growth process. To mimic the real micellar system, \( \Delta E \) is assumed to include the chemical potential, \( \mu \), and the interaction potential, \( V \), gained when the candidate site is occupied. The following interaction potentials associated with different entities in the structure can be subsumed into \( V \) (Fig. 2.21): (1) \( J_e \), associated with every edge of the tiles; (2) \( J_r \), with every right angle formed by two edges; (3) \( J_t \) or \( J_s \), with every triangle or square, respectively; (4) \( J_{ss} \), \( J_{st} \) or \( J_{tt} \), with every contact between two tiles; and (5) \( J_{ttt} \), with every cluster of three triangles ("s" and "t" in the subscripts stand for "square" and "triangle", respectively). In total, \( V \) is calculated as the sum of all the interaction terms for the entities newly generated by occupying the candidate site.

A survey of the above parameters sheds light on the primary factors that cause a systematic change in simulated structures. It turns out that unlimited aggregation of triangles can be avoided only if repulsive interactions are assumed between adjacent triangles; that is, \( J_{tt}, J_{ttt} > 0 \). Importantly, transformations from \( 3^2.4.3.4 \) to a dodecagonal twin-like arrangement of \( 3^3.4^2 \) and further to a quasicrystalline tiling are reproduced by reducing these repulsive interactions (Fig. 2.21), keeping the other parameters constant. This is in accord with the experimental finding that these transformations occur through a small decrease in alkalinity, and thus each entity (edge, right angle, square, triangle) presumably maintains the same degree of stability. The repulsions between triangles can possibly be attributed to the interfacial energy between the micelles. In a soft micellar aggregate, the total interfacial area can be reduced by expanding higher-coordinated cells against their lower-coordinated neighbours. Thus, if a cell having the highest coordination, \([5^{12}6^3]\), is surrounded only by lower-coordinated neighbours, it will expand to adjust its size so that the interfacial force is balanced by the micellar elasticity. If the adjacent neighbours also include highest-coordinated cells, which happens when triangles are in con-
**Figure 2.21:** a, A graphical presentation of the interaction potentials in the model. b–d, The simulated tiling obtained with the common parameters of $p_0 = 0.01, \mu/T = -0.0008, J_c/T = -0.0004, J_r/T = -0.0002, J_e/T = J_t/T = J_{ss}/T = 0, J_{st}/T = -0.0008$ and the following input parameters: $(J_{tt}/T, J_{ttt}/T) = (0.0004, 0.00002)$ for b, $(0.00027, 0)$ for c, and $(0.00012, 0)$ for d. Panel c shows signs of the dodecagonal morphology with 12 fans. In d, the centres of dodecagonal wheel motifs, which are shaded light grey, are indicated by open dots. Connecting the dots with edges of length $2 + \sqrt{3}$ reveals larger squares and triangles, whose divisions demonstrate the inflation rules for the Stampfli tiling. Insets at top right show the Fourier transform of each pattern. The numbers of triangles and squares in b, c and d are respectively $(1424, 709)$, $(1452, 689)$ and $(1507, 668)$.

In contact, the expansion is suppressed; therefore, a direct contact between triangles carries a cost in interfacial energy.
2.6.2 Pair potential

Another simply investigation excluding the three body interaction is to express the $\Delta E$ by a pair-potential $v(r)$ between an arbitrary pair of vertices in the tiling patch, where $r$ stands for the distance between the vertices. Thus $\Delta E$ is calculated as $\Delta E = \sum_{<i,j>} v(r_{ij})$, in which $<i,j>$ runs over all the pairs of occupied vertices in the patch. The values of $v(r)$ at selected distances between a pair of vertices are important; these distances include $r_1 = 1$, $r_2 = \sqrt{2}$, $r_3 = \sqrt{3}$, $r_4 = \sqrt{2+\sqrt{3}}$, $r_5 = 2$, $r_6 = \sqrt{5}$, as well as $r_0 = \sqrt{2-\sqrt{3}}(<1)$, which corresponds to the short diagonal of a 30 degree rhombus (Fig. 2.22 (a)).

A peculiar type of the force field with double minima and a positive barrier in between successfully reproduces the characteristics of our samples. A positive barrier at $r_3$ is essential to avoid an unlimited growth of the tiling $3^6$, just as the assumption of $J_{tt}, J_{ttt} > 0$ in the model above, while a negative well at $r_4$ is still needed for configurations like $3^3.4^2$ to form in a stable manner. Moreover, reducing the magnitude of the oscillatory feature in the tail of $v(r)$ (Fig. 2.22) enhances competitions between different configurations of squares and triangles, thereby the random tiling at the center becomes more prominent. This effect is similar to decreasing the $J_{tt}$ and $J_{ttt}$ in the model above. The tiling $3^2.4.3.4$ can be grown in a stable manner only if the oscillation in $v(r)$ is strong and the ratio $v(r_5)/v(r_4)$ is small (Fig. 2.22).

2.6.3 Explanation of the simulation results

Although through different approaches, both simulation above have the common feature that reduced repulsion between triangles facilitate the random configuration of squares and triangles that leads to the quasicrystalline pattern. Considering the 3D polyhedron model corresponding to the 2D square-triangle tilings, the simulation explains our experimental results obtained at different alkalinity conditions: A higher pH led to an increased electrical charge density of the surfactant heads and of the silica sources. The enhanced intra-layer Coulomb interactions at higher ionization would promote the stability as well as the flexibility of the interface layer [18]; the expansion of the highest-coordinated cells would thereby be facilitated, leading to an enhancement of repulsions between triangles. The $P4_2/mnm$ structure provides the highest stability at the highest pH with an interwoven of squares and triangles. If the repulsions between triangles were suppressed by reducing the alkalinity, the energy difference between triangles and squares are reduced and they can be more randomly tiled, resulting in the growth of a multiply-twinned-like structure. Further reducing the alkalinity would maximize the competition between triangles and squares, leading to a random configuration of them. This is what
we observe in the central part of our material. These adjustments require only a slight change of alkalinity; therefore, a fine-tuning of the alkalinity is at the heart of further improvement of the quasicrystallinity. However even further reduction of alkalinity makes $[5^{12}6^3]$ polyhedra no longer favoured, as the $Pm\tilde{3}n$ structure would then be superior.
Figure 2.22: Results of growth simulations assuming pair potential $v(r)$ with $(v(r_j)/T)_{j=0,1,..,6} = (0.016, -0.00252, -0.00088, \xi_1, \xi_2, \xi_3, 0)$, in which three sets of values for $(\xi_1, \xi_2, \xi_3)$ are used. (a) The normalized pair-potential parameters $v(r_j)/T$ at the seven distances are displayed with interpolation curves of cubic-spline, illustrating the double-well nature of the pair potential. The correspondence of $r_1 - r_4$ to the 2D tiling is inserted for clearance. The three sets of values for $(\xi_1, \xi_2, \xi_3)$ are: (b) $(0.00168, -0.00112, -0.00048)$, (c) $(0.0012, -0.0008, -0.0006)$ and (d) $(0.001, -0.00056, -0.0004)$. (b,c,d) Tilings grown from a screw shaped seed patch (the gray part in the center of each tiling) for the three set of parameters. Their boundary loops are shown by thicker curves, while the candidate sites by dots. The panel (c) shows a sign of the dodecagonal morphology with twelve fans. The Fourier transformation of each pattern is inserted as subfigure. The number of triangles and squares are (1440, 698), (1454, 697) and (1500, 668) for tilings in (b), (c), (d) respectively.
3. Minimal surface transformation of mesoporous silica

3.1 Minimal surfaces in mesoporous silica

![Figure 3.1](image)

**Figure 3.1:** The graphic demonstration of the principle curvatures, with the surface curves corresponding to the positive ($\kappa_1$) and negative ($\kappa_2$) curvatures drawn on the surface.

Minimal surface is defined as the surface with constant zero mean curvature everywhere on the surface. The mean curvature is described by the two principal curvatures, which are the maximum and minimal curvatures of the surface curves that can be extracted from a point on the surface, denoted as $\kappa_1$ and $\kappa_2$ (Fig. 3.1). The average of the principal curvatures gives Mean curvature $H$ at that point: i.e. $H = \frac{1}{2}(\kappa_1 + \kappa_2)$. Physically, the minimal surfaces are locally surface minimizing, so that in general soap films are minimal surfaces if the gravity is neglected [36].

When the minimal surfaces have crystalline structures it is called triply periodic minimal surface. Three kinds of minimal surfaces are commonly observed to have counterparts in mesoporous materials: D, G and P minimal surfaces (Fig. 3.2). The counterparts to G and D surfaces are commonly referred to as bicontinuous structure, because they form continuous bilayers as oppose to discrete micelles. The bilayer of either G or D again form two identical but independent channel systems twisted with each other. Normally the bicon-
Continuous structure is found to be in between lamellar and hexagonal columnar structures, because the surfactant packing parameter $g$ for these structures are in the range of $1 \sim 1/2$. The examples of the structures are MCM-48 [35] and AMS-6 [28] for G with space group of $Ia\bar{3}d$, AMS-10 [25] for D with space group of $Pn\bar{3}m$, and a metal oxide containing mesoporous silica from a block copolymer-hybrid mesophase for P with space group of $Im\bar{3}m$ [20]. Not only in the family of mesoporous materials, surfactants and other membrane systems such as endoplasmic reticulum also possess the favor to stabilize in the bicontinuous cubic phases, possibly for their surface area minimization and close-to-constant curvature features.

### 3.2 Transformations among minimal surfaces in mesoporous silica

The structure transformation among the three minimal surfaces are ubiquitous, for they are topologically equivalent and can be inter-converted by several smooth processes [63]. The first one, Bonnet transformation [36], is mathematically important, since it preserves the Gaussian curvature at any point on the surface during transformation. Other geometric parameters are also preserved such as angles, distances and areas on the surface. However this transformation method is unlikely to happen in real cases since it requires parts of the minimal surface to pass through each other. For bilayer it means to be torn apart and then joined back, which is energetically unfavourable. Another one, which derives from the topology equivalence of the surfaces that they can be transformed into one another without tearing the bilayer, utilizes the relationship of the junctions for different structures. By merging two adjacent three-way junctions, one can transform G surface into D, while merging two adjacent four-way junctions of D can produce P [63]. This method is not only conceptually easy but also physically meaningful. Beside the structure
transformation among the minimal surfaces, hexagonal columnar structure is also an candidate which is closely related to G surface by transformation. The transformation from the columnar to G structure may induce some intermediate structures as modeled by Matsen [48].

The transformations above have their counterparts in systems like hydrated lipid system [63]. However the experimental methods so far are not adequate to distinguish exactly the mechanism for the structure transition. In mesoporous silica system, g parameter is used as a rough explanation for the structure versatility [26], while the detailed transformation still needs more careful work. The condensation of silica wall besides thermal excitation of surfactant hydrophobic tails is also suspected to play a role in Cylinder to Gyroid transition during Hydrothermal treatment [4], which adds more thought as well as complexity to understand the transition mechanism of mesoporous silica materials.

3.3 Structural transformation between G and D induced by TMB

Normally tri-methyl benzene (TMB) is used as the swelling agent to increase the size of mesopores, as the hydrophobic feature of the TMB directs it to stay at the tail part of the surfactant molecules. The accompanying increase of the tail volume can increase the surfactant packing parameter $g = \frac{V}{a_0 l}$, possibly leading to a phase transformation. In the synthesis based on Reference [4], we have obtained a structure transformation from 2D hexagonal to bi-continuous $Ia\bar{3}d$ by increasing the TMB amount in synthesis. Interestingly, a further increase of TMB has triggered a structure transformation from $Ia\bar{3}d$ to $Pn\bar{3}m$, which corresponds to G to D minimal surface transition. Electron Microscope and Small angle X-Rays (SAXS) are used to track the structural shift during the addition of TMB, and investigate the transformation at certain point, trying to understand the mechanism behind this process. Moreover, a kinetic and hydrothermal synthetic study is performed around the composition where structure transformation happens, in order to determine which phases are dominant as well as to determine the epitaxial relation between mesophases.

3.3.1 Synthesis

A homogeneous solution of surfactant $C_{12}AlaA$ was obtained in distilled water at $80^0C$ for 24h under static conditions. Tri-methyl benzene (TMB, Sigma-Aldrich), was added to the surfactant solution and was stirred for 1 hour at $80^0C$ in a closed bottle before addition of co-structure directing agent (3-aminopropyl)triethoxysilane (APES). TEOS was added 2.5min after APES. The solution was stirred for another 15 minutes at $80^0C$ in a closed bottle. The
synthesis gel was subsequently stored at room temperature under stirring conditions for 24h. The final synthesis mixture was kept sealed at 100°C under static conditions for 2 days. The solid product was filtered and dried at Room temperature and under atmospheric pressure conditions. The molar composition of the reaction mixtures was $C_{12}\text{Ala} : \text{APES} : \text{TEOS} : H_2O : \text{TMB}= 1 : 1.25 : 6.7 : 309.1 : x$. Samples are denoted AMS-6(x) where x denoted the molar ratio of $\text{TMB}/C_{12}\text{Ala}$ in the synthesis gel.

### 3.3.2 XRD characterization

Powder X-ray diffraction is used to identify the structure transformation and for the accurate structure factor intensity free from multiple scattering that often exist in TEM characterization. The measurements were performed at BL02B2 in a synchrotron radiation facility SPring-8 (Japan) using a wavelength of 0.100 nm. The powder specimen was mounted in Lindemann glass capillary (diameter = 0.4 mm). The XRD profiles were recorded using an imaging plate set into a Debye-Scherrer type detector. Si fine powder (NIST SRM 640d) was used as the internal standard to calibrate an origin of XRD pattern and the wavelength at each measurement. In order to extract the integrated intensities of Bragg reflections, the observed XRD profiles were analyzed by Pawley fitting with split-type Pearson VII function implemented in TOPAS-academic refinement program.

From the XRD pattern we could see that starting from the $\text{TMB}/C_{12}\text{Ala}$ molar ratio of 5, the increase of TMB amount only increase the unit cell size of $Ia\overline{3}d$ structure and no structure transformation was obtained until the ratio of 57, where there is a sudden decrease of the unit cell size (Fig. 3.3). From $\text{TMB}/C_{12}\text{Ala}$ molar ratio of 56, the increase of TMB swells the unit cell again until AMS(64), where another distinct peak appears, which can be indexed on the basis of the $Pn\overline{3}m$ symmetry (Fig. 3.4). The emerging structure of $Pn\overline{3}m$ is further confirmed by TEM, as shown in Fig. 3.5. Interestingly, there are some intermediate peaks for sample AMS(58) and AMS(60), which cannot be indexed by either $Ia\overline{3}d$ or $Pn\overline{3}m$ space groups. They can be assigned to the intermediate structure between G and D, although TEM observation has not seen able to identify it possibly due to the relatively small proportion of the intermediate phase in the samples.

### 3.3.3 EM observation

TEM observation has been done to investigate the samples during structure transformation, i.e. AMS(64). Although both structures exist in this synthesis condition, most of the samples show pure $Ia\overline{3}d$ or $Pn\overline{3}m$ structures, as can be seen from Fig. 3.5. However, few particles also show a epitaxial relation
Figure 3.3: The XRD pattern of as-synthesized samples of AMS-6 with TMB/C_{12}Ala ratio from 5 to 57 (X-ray wavelength 0.100nm). All these patterns can be indexed by Ia\bar{3}d with 211 and 220 indices of it marked.

between G and D phases, especially on the boarder of the particle, as can be seen in Fig. 3.6. The epitaxial relation occurs between the [111] orientation of Ia\bar{3}d mesostructure and the [110] of the Pn\bar{3}m structure, where the associated reflections are the 220\text{I} and 200\text{P} as observed from the FFT. Interestingly the d-spacing for these reflections are not exactly the same, with \(d_{220\text{I}} = 70.0\text{Å}\) and \(d_{200\text{P}} = 72.0\text{Å}\)

Previous observation shows that there is a thin layer of pores surrounding the external particle surface [4], and it is assume to be the epitaxial growth layer during synthesis with no blockage of the pores. In our samples we also observed the surface features, as shown in Fig. 3.5 and Fig. 3.6. Moreover, there is an uneven contrast at the sample part of the TEM images, which looks like the thickness contrast. It is suspected then that the particles have a uneven morphology. This is confirmed by SEM (Fig. 3.7), from which we can see that the particle loses its integrity with numerous surface features. These microscope results indicate the dissolution may be involved in the synthesis as well as the structure transformation process.
3.3.4 A mechanism investigation- kinetic study

Due to the observation of the dissolution clue, we performed a kinetic study for the structure transformation to investigate the time dependence of the structure. Hydrothermal treatment (HT) is also introduced to compare with the result without HT to see the role of HT and we found that at different temperatures (with or without HT) the stable structure differs. The kinetic study was performed at a TMB/surfactant ratio of 64 where structure transition can be triggered. Mesoporous samples were obtained after 6, 18, 24, 48, and 120 hours of synthesis at room temperature (RT) without HT; and with HT for 6, 48 and 64 hours after 24 hours of synthesis at RT. The structures obtained along the kinetic process is summarised in Fig. 3.8 and the corresponding XRD patterns are shown in Fig. 3.9.

From Fig. 3.9 it can be seen that the crystalline structure is originated from
Figure 3.5: TEM images and corresponding FFT pattern of the particles synthesized at the condition of AMS(64) with space groups of (left) \( Ia\overline{3}d \) and (right) \( Pn\overline{3}m \).

hexagonal columnar structure which can be indexed at synthesis time of 18h. With prolonged synthesis time under RT, the structure transforms into \( Ia\overline{3}d \) and is stable until after 48h while the sample obtained at 120h can already be indexed based on \( Pn\overline{3}m \) space group. Further TEM observation has found that at 24h, there is small amount of \( Pn\overline{3}m \) and the amount increases with increasing synthesis time, until at 120h, the \( Ia\overline{3}d \) structure serves as a minor structure. The samples with HT undergoes a different structure transformation process, as can be identified from Fig. 3.9. The structure begins with \( P6mm \) with HT of 6h and then maintains \( Ia\overline{3}d \) until at the HT of 48h, where another peak can be clearly seen that correspond to the 110 of \( Pn\overline{3}m \) structure. However this transformation didn’t continue to end up with the newly emerged \( Pn\overline{3}m \) but went back to \( Ia\overline{3}d \) after HT of 64h. TEM observation found that the structures are a mixture for all the samples, however XRD in most cases can only identify the major structure in a mass. Fig. 3.8 gives a more precise and clear conclusion of the structures at stage of the kinetic process.

Similar kinetic study of AMS material has been performed by Rambabu Atluri et al [4]. The synthesis procedure is similar however without addition of TMB. Under HT the structure changed from hexagonal columnar \( P6mm \) to bicontinuous \( Ia\overline{3}d \) and then back to \( P6mm \). There is no appearance of \( Pn\overline{3}m \) although their kinetic study. Thus we can see, although time is an important parameter to trigger structure transformation, TMB is a must to lift \( Pn\overline{3}m \) into the group of structures being transformed. The effect of time originates from the hydrolysis of silica precursors and the degradation of the surfactant, as discussed in Reference [4], while the role of TMB is normally swelling the pore of the materials. From our experiment, the TMB also offers as an agent to
Figure 3.6: The epitaxial relation between the $Ia\bar{3}d$ or $Pn\bar{3}m$ structures in the particles synthesized at the condition of AMS(64). The main orientation of the particle is along the [110] orientation of the $Pn\bar{3}m$ structure. However on closer inspection the edge of the particle possess a layer of the $Ia\bar{3}d$ structure of approximately 3 unit cells. Two regions in the particle possess the epitaxial relation, marked by a white box on the sub-figure in the right bottom. FFT reveal that the coincidence reflections are the 440 and 400 of the $Ia\bar{3}d$ and $Pn\bar{3}m$ symmetry structures respectively.

lower the barrier energy of the $Pn\bar{3}m$ structure. Moreover, the HT process does not only accelerate the condensation of the silica wall, but also offers different stable states for the structure transformation, since at different temperatures, the transformation process ends at different structures. In our case, the $Ia\bar{3}d$ structure is more stable at RT while HT makes $Pn\bar{3}m$ more stable.

3.3.5 Trials in accurate 3D reconstruction

In order to understand the role of TMB in the structure transformation, reconstructed models are necessary that follow the series of samples with increasing amount of TMB during synthesis. There are several ways to reconstruct such models, each having its pros and cons. Several approaches were tried in the project and are discussed below.

For each AMS material, reconstruction is performed following the procedure described in Fig. [I,II] from which we can get the electron density map of the materials. However, the particle size of our samples is too small to break under crushing, while the particle dimension is a little too large (~100nm in diameter) to get the images free from multiple scattering. In this case we con-
Figure 3.7: (left) TEM and (right) SEM images showing evidence of particle surface dissolution. Both images are recorded from sample AMS-6(52). The lighter contrast zones in left image corresponds to the surface porosity clearly visible in the right image.

Considered XRD results with less multiple scattering problem. Since both XRD and TEM reflect the electron states of the crystal, with XRD giving electron population density and TEM providing electrostatic potential distribution inside crystal. They can be connected by Mott formula of

\[ f_e(g) = \frac{e}{4\pi\varepsilon_0} \left( \frac{Z-f_X(g)}{\pi g^2} \right), \]

where \( f_e \) and \( f_X \) are the electron scattering factor and X-ray scattering factor respectively [23].

Seen from Fig. 3.3, only two peaks are observable even using the synchrotron source, which is mainly due to the inherent deviation of both lattice and pores of the mesoporous silica materials. Thus we uses only the first two peaks to integrate the amplitude of the structure factors, while the phase of the structure factors are determined from TEM images. After application of the contrast transfer function (CTF) and recombination of 3D structural data, 3D electron density map can be obtained from inverse FFT.

A further step after obtaining electron density map is to determine the threshold of it so that we can get an isoelectronic density surface, which is used as the representation of the boundary between the channels and the silica wall. For calcined sample, this step is normally done by measuring the pore volume of the material by gas-adsorption-desorption measurement, and using it as a criteria for the model. However during calcination, a further condensation of silica wall will proceed so that the silica wall will go through a significant shrinkage, which means the structure after calcination cannot accurately reflect the real structure as synthesized. For our purpose of understanding the structure transformation mechanism from progressive tiny structural changes, minimized distortion from the original shape is desired, which means as synthesized samples are favoured. However, for samples without calcination or extraction, the mesopore volume is not attainable. Keiichi Miyasaka et al. have
developed a self-consistent method to determine the threshold of the electron potential map [51]. In this method they rely on the structure determination parameter of minimization of the Helfrich energy, which effectively take the isoelectric density surface with least variation in curvature. Our trial using this method gave reasonable structures however the accuracy is not enough to reflect the structure transformation trend by increasing TMB amount. Since TMB is well known to be swelling agent, more swelling of the pores should coexist with more TMB, which can be used as a rough criterion to judge the accuracy of the threshold determination method in our case. The failure of the method in our case may be because of existence of other mechanism besides the curvature energy term.

To eliminate the uncertainty brought by assumptions of material structure, a criteria based on experimental result would possibly be more reliable. We thus chose the diffraction peaks’ amplitude ratio of Amp(211)/Amp(220) obtained from XRD as a criteria, and obtain the structure model by approaching its simulated structure factor amplitude ratio as close as possible to the experimental result. However, this method gives quite unbelievable result with large structure fluctuation with increasing TMB amount. This may be induced by
The rough assumption during simulation that the silica wall has even density which is actually not due to that different amounts of TMB hinder the silica hydrolysis and condensation process to different extent. The surface roughness is also another uncertain factor that affects the simulated structure factor profile.

In the two trials above, a guide line can be concluded: less assumption produces more accurate result. For this we have to go back to the classical method of using gas-adsorption-desorption method, since the pore volume is an experimental criteria instead of assumption. To minimize the distortion from the original structure, extraction is performed instead of calcination, as extraction does not heat the sample too much (70°C during extraction). To make sure the surfactant was fully extracted, the extraction was repeated twice for each sample. By comparison with the original sample, the unit cell size of the extracted sample has a shrinkage of around 5Å (Table 3.1), i.e., about 5% of unit cell size, and the basic structure does not show any sign of change. Based on the pore volume measured from the extracted samples, reconstruction process
was performed and the result shows a reasonable trend of increasing pore size with increasing TMB amount in synthesis. The results from the reconstructed structure models are shown in Table 3.2.

<table>
<thead>
<tr>
<th>sample</th>
<th>unit cell size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5_as</td>
<td>12.7</td>
</tr>
<tr>
<td>7.5_ex</td>
<td>12.3</td>
</tr>
<tr>
<td>8.1_as</td>
<td>12.8</td>
</tr>
<tr>
<td>8.1_ex</td>
<td>12.5</td>
</tr>
</tbody>
</table>

**Table 3.1:** The comparison between the unit cell size of the extracted samples and that of the as-synthesized samples, showing that the shrinkage is in an acceptable region

<table>
<thead>
<tr>
<th>TEM/surf. ratio</th>
<th>pore volume ($cm^3/g$)</th>
<th>unit cell size (nm)</th>
<th>pore diameter along [111] (nm)</th>
<th>wall thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.45</td>
<td>11.7</td>
<td>3.4</td>
<td>2.1</td>
</tr>
<tr>
<td>20</td>
<td>0.53</td>
<td>11.8</td>
<td>3.3</td>
<td>2.2</td>
</tr>
<tr>
<td>52</td>
<td>0.69</td>
<td>13</td>
<td>3.4</td>
<td>2.7</td>
</tr>
<tr>
<td>58</td>
<td>0.45</td>
<td>12.7</td>
<td>3.6</td>
<td>2.3</td>
</tr>
<tr>
<td>60</td>
<td>0.50</td>
<td>12.8</td>
<td>3.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

**Table 3.2:** The structural information from samples synthesized with different TMB amount
4. Structure study on surfactant liquid crystals

4.1 The difference between liquid crystal and mesoporous silica

Mesoporous silica materials are commonly depicted as a nano-structured form of silica templated by surfactant micelles, and the discussions on the structure-forming mechanism of mesoporous silica is quite often quoting the principles of surfactant liquid crystals. However, there are some essential differences between the formation of surfactant liquid crystals and that of mesoporous silica. First of all, the formation of mesoporous silica materials is considered to be a kinetic process, which involves the hydrolysis and condensation of silica precursors. The interaction of silica precursors and the surfactant micelles are essential for the crystalline structure to form at surfactant concentrations well below the Critical Micelle Concentration (CMC), which is commonly known as the cooperative self-assembly process [21]. The structure is not only determined by the configuration of the surfactant molecules but also largely dependent on the conditions of the silica oligomers, which may lead to a structure transformation during the condensation process of the silica precursors [52]. Moreover, the inclusion of CSDA in anionic surfactants imposes another freedom in the structure evolvement: it both acts as an extension of the surfactant headgroup and also join the formation of the silica frameworks. On the other hand, the structures of surfactant liquid crystals are thermodynamically stable, and are fully dependent on the surfactant configurations at certain temperature and concentrations in binary systems (i.e. a mixture of one kind of surfactant and one kind of solvent). Thus the theoretical consideration on the liquid crystal system is easier to conduct and in principle more reliable, which could in turn work as a basis for understanding the mesoporous silica forming process.

4.2 Parameters affecting the structure of liquid crystal

Although the system is compositionally simple compared with that of the mesoporous silica synthesis, in order to understand the forming mechanism
of various liquid crystal structures, the affecting parameters need a clear cataloguing. First of all, the origin of self-assembly is needed in order to understand how the surfactant form micelles whose sizes are constrained in a narrow range. Based on this, the short-distance forces between surfactants and micelles come into play and affect the final structure of the liquid crystals. These forces originate differently and locate in different parts of the surfactants or micelles, thus are quite often affected differently by the controllable environmental parameters, whose variation constructs the phase diagrams that normally composed of several different structures.

4.2.1 The thermodynamics of self-assembly

As the surfactants are thermodynamically stable in the solution, their chemical potentials should equal to each other. Let’s consider the case that identical surfactants aggregate differently, *i.e.* they are in micelles of *N* surfactant molecules. Their chemical potential can be expressed as:

\[ \mu = \mu_N = \mu_0^N + \frac{kT}{N} \log \left( \frac{X_N}{N} \right) = \text{constant}, \quad (N = 1, 2, 3, \ldots) \]  

where \( \mu_N \) is the mean chemical potential of a molecule in an aggregate of *N* molecules, \( \mu_0^N \) stands for the mean interaction free energy per molecule, and \( X_N \) the concentration of molecules in aggregates of number *N* (\( X_1 \) corresponds to isolated molecules). This equation serves as the basis for the following considerations.

### formation of aggregates

Aggregates form in solution means a reduction of chemical energy when molecules assemble together, or in another word, the exposure of some “molecular surface” is unfavourable in solution, the bonding between molecules reduces the total energy. A simple consideration is the aggregation of molecules into a string, where the “bonding energy” between molecules are set to \( \alpha kT \). An aggregate of *N* molecules are connected by *N*-1 “bonds” and has a total interaction free energy of \( N \mu_0^0 = -(N-1) \alpha kT \), which is:

\[ \mu_0^N = -(1 - 1/N) \alpha kT = \mu_0^\infty + \alpha kT / N \]  

from which we can see the mean free energy decreases asymptotically with increasing *N* towards \( \mu_0^\infty \), the energy of a molecule in an infinite aggregate.

If the aggregate is in 2D or 3D form, the dependence of \( \mu_0^N \) on *N* is different. For example the number of unbounded molecules is proportional to
the circumference $2\pi R$ and the area $4\pi R^2$ respectively, i.e. $N^{1/2}$ and $N^{2/3}$ respectively, to the 2D disc and 3D sphere aggregates. Thus we could get $\mu_N^0 = \mu_\infty + \alpha kT / N^{1/2}$ and $\mu_N^0 = \mu_\infty + \alpha kT / N^{1/3}$ respectively for them. From these examples we could see, in general, for simple shaped structures, the interaction free energy of the molecules can be expressed as:

$$\mu_N^0 = -(1 - 1/N)\alpha kT = \mu_\infty + \alpha kT / N^p$$  \hfill (4.3)

where $\alpha$ is a positive constant depending on the intermolecular interactions and $p$ is a number depending on the shape or dimensionality of the aggregates. A positive $p$ means a decreasing free interactive energy with increasing $N$, i.e., which is a necessary condition for aggregate formation.

This beads model is an over-simplified model for self-assembly, however it serves as a thermodynamic basis for further consideration of more practical cases.

**CMC**

The formation of the aggregates require the solute to reach some critical micelle concentration (CMC). How the concentration comes and the theoretical value can be understood based on the beads model above. From Equation (4.1) we could get the expression of the aggregate concentration $X_N$:

$$X_N = N\{X_1 \exp[\alpha(1 - 1/N^p)]\}^N \approx N[X_1 e^{\alpha}]^N$$  \hfill (4.4)

For sufficient low concentration $X_1$, $X_1 \exp[\alpha(1 - 1/N^p)]$ or $X_1 e^{\alpha}$ is much less than unity, we could see that the concentration of the solute in aggregates of number $N$ decreases in the power of $N$, i.e. most molecules in the solution will be isolated and $X_1 \approx C$. Increase of the total molecule concentration $C$ increases the $X_1$ almost linearly at low concentrations. However, since the $X_N$ must be less than 1 and thus from Equation (4.4) the $X_1$ value cannot be more than $\exp[-(\mu_1^0 - \mu_N^0)/kT]$ or $e^{-\alpha}$. This critical concentration $(\exp[-(\mu_1^0 - \mu_N^0)]$ or $e^{-\alpha})$ of $X_1$ is just the CMC. For now we denote it as $(X_1)_{crit}$.

Now let’s put $(X_1)_{crit}$ back into Equation (4.4) to see how it will develop at or above this concentration:

$$X_N = N[X_1 e^\alpha]^N e^{-\alpha N^p}$$  \hfill (4.5)

Depending on the value of $p$, the equation develops differently. For $p < 1$, above $(X_1)_{crit}$ we get $X_1 e^\alpha \approx 1$ and the equation becomes $X_N \approx N e^{-\alpha N^p}$. At a reasonable positive value of $\alpha$, the function behaviour with $N$ can be
understood intuitively by applying the model of disc $(p = 1/2)$ or sphere $(p = 1/3)$, in both cases the $N$ value can hardly be larger than 5 constrained by the fact that $X_N$ cannot be larger than unity. This means there can be few aggregates of any appreciable size (e.g. $N > 5$). So the additional molecules after the concentration reaches $(X_1)_{crit}$ have nowhere to go but separate out from the solution, or in another word, aggregate with $N− > ∞$ forms above $(X_1)_{crit}$ if $p < 1$. This condition of $p < 1$ corresponds to the beads model discussed above, which can be associated with molecules that are hydrophobic at all edges or faces, like oil and alkane molecules. These molecules will separate from the solution to form bulk oil phase when they reach the critical concentration.

If $p > 1$, $X_N = \frac{NX_1}{e^{\alpha(Np-N)}}$, from which we could see no appropriate aggregate can be formed since an reasonably $N$ larger than 1 gives small $X_N$ value. This is physically not meaningful and will not be considered here.

Thus we could see that a $p$ value larger or smaller than unity cannot form notable aggregates of finite sizes. The only possibility is to consider the case where $p = 1$. In this case Equation (4.5) becomes

$$X_N = N[X_1 e^\alpha]^N e^{-\alpha}$$

(4.6)

In order to obtain the dependence of $X_N$ on the $N$ value, we need to substitute the unknown $X_1$ value by some know expressions. For this let’s consider the concentration $C$:

$$C = \sum_{N=1}^{\infty} X_N$$

(4.7)

$$= \sum_{N=1}^{\infty} N[X_1 e^\alpha]^N e^\alpha$$

$$= X_1/(1-X_1 e^\alpha)$$

from this the $X_1$ can be expressed by the concentration $C$ as:

$$X_1 = \frac{(1+2Ce^\alpha) - \sqrt{1+4Ce^\alpha}}{2Ce^\alpha}$$

(4.8)

since we are considering the concentration at or above CMC, the $C$ value should be large so that $Ce^\alpha \gg 1$, which gives $X_1 \approx (1-1/\sqrt{Ce^\alpha})e^{-\alpha}$, putting this back into Equation (4.6) we get:

$$X_N = N(1-1/\sqrt{Ce^\alpha})^N e^\alpha$$

(4.9)

$$\approx Ne^{-N/\sqrt{Ce^\alpha}} (for large N value)$$

88
The function peaks at $\frac{\partial X_N}{\partial N} = 0$, which is at:

$$N_{\text{max}} = M = \sqrt{Ce^\alpha} \quad (4.10)$$

we see this distribution is a function of the molecule concentration as well as the interaction parameter $\alpha$, meaning the aggregate number and the polydispersity is sensitive to concentration, temperature, electrolyte concentration etc. The above derivation proves that at $p = 1$ the aggregates of finite value can be formed. This specific value can not be obtained by the simple beads model, as the $p$ value is smaller than unity and will cause a phase separation like oil and alkane molecules. The molecules in this case needs to be more flexible, where the energetically unfavourable regions at the end of rod like aggregate may be eliminated by bend or join together. This is where the amphiphilic molecules come into play, such as surfactant. In this case the chemical potential does not decay gradually with increasing $N$, as in Equation (4.1), rather it reaches an minimum at some finite value of $M$.

### 4.2.2 Forces in the liquid crystals

In order to understand the factors that determine the ultimate structure of liquid crystals, two kinds of interactions must be taken into account: between aggregates and inside the aggregates. The first affect largely the arrangement of micelles, while the latter drives the shape of each micelle. However these two groups of interactions cannot be completely separated as both essentially affect components of micelles, *i.e.* surfactants.

**Interaction between aggregates**

From the ultimate effect, we categorize the forces into two groups: repulsive and attractive. The repulsive force comes from the electrostatic, steric or hydration forces, while attractive force comes from Van der Waals force or electrostatic forces generated by zwitterionic headgroups or from a screen effect.

In the case of repulsive force, above CMC, when the concentration of solute is increased, the already formed micelles are forced to come closer to each other. To minimize the increased repulsive forces by this distance decrease between micelles, the surfactants need rearrangement so that the repulsive micellar surfaces get further apart from each other. For this purpose periodic arrangement of the micelles into cylinders are quite often obtained. At a further increased concentration, the stack of bilayers may form to reduce the intermicellar surface areas. Quite often these bilayers form analogies of periodic minimal surface to minimize the exposed surfaces.

The case of attractive force is more complex, as there exist a competition between higher entropy of small micelles and lower interactive energy of large
liposomes. The solution may form small micelles at concentration higher than CMC, while a further increase of the concentration may force the attractive micelles to aggregate together to form even larger liposomes. We can contrast this process by considering two CMCs: first for the monomers to aggregate into micelles and second for the micelles to merge into liposomes.

**intra-micellar forces**

The forces that act on different parts of surfactant molecules are different inside the micelles. At the interface between the hydrocarbon chains and the water, an attractive interface tension exist to minimize the contact of water and the hydrocarbon chains, also known as hydrophobic attraction. On the contrary, slightly outside the interface, where the headgroups of surfactant molecules locate, repulsive forces such as steric, hydration and electrostatic double-layer forces repel the headgroups from coming close to each other. These two contradicting forces are most predominantly considered in determining the shape of the micelles, while the hydrocarbon chains are normally assumed to be fluid. However, the chains are never perfectly fluid and also posses interaction with each other, the steric repulsion between them contribute a effective lateral chain pressure inside the hydrocarbon region. These forces at the three parts of micelles act together to determine the shape and curvature of the micelles. Their impact can be varied depending on the environment conditions like temperature, surfactant concentration etc.

**The role of temperature and concentration**

The temperature change can have effect on both the headgroup and chain part. Increasing temperature would increase the hydrocarbon chain motion involving trans-gauche isomerization and thus reduces the chain length. Depending on the characteristic of the headgroups, the temperature change could have different effects. In general, with increasing temperature non-ionic spherical micelles grow in size and become more cylindrical, while charged micelles shrink.

The effect of concentration was discussed before for the interaction between aggregates. The basic idea is that at higher concentration the surfactants need to rearrange in order to minimize their inter-facial reaction (repulsive), thus normally structures having a lower surface-to-volume ratio is desired.
4.3 Structures of liquid crystals from surfactant $C_{14}GlutANa$

(This section is mainly originated from the paper VII attached at the end of the thesis. A short description is put here for the consistency of the thesis.)

In the family of surfactants that are used in mesoporous silica materials, the anionic surfactant has attracted special interest for the diverse structures it can produce just by varying synthesis conditions [26]. Beside some typical structures that can be synthesized by cationic and non-ionic surfactants, the anionic surfactant possesses the uniqueness in obtaining several special structures, such as the bicontinuous structure mimic the minimal surface D [25] and recently a dodecagonal quasicrystalline structure [74]. However, the specialty of the surfactants in synthesizing various structures is shielded by the kinetic cooperative self-assembly growth process where the silica oligomer also plays an important role in addition to the surfactant [21, 27]. The necessity of using CSDA for anionic surfactants in synthesizing the mesoporous silica has added another complexity in understanding the surfactant-related mechanism of forming these various structures. Thus, investigating the liquid crystalline phases of this kind of surfactant could serve as a thermodynamically stabilized basis for further discussion on the structure forming mechanism involving the CSDA and silica precursors. Bearing this in mind, we performed the structural study of the liquid crystals formed by the anionic surfactant Sodium N-Myristoyl-L-Glutamate ($C_{14}GlutANa$), which has successfully produced a large variety of mesoporous silica structures just by changing synthesis conditions [26]. Various structures are formed, including lamellar, 2D-hexagonal and cubic $Pm3n$ structure, which are also obtained in mesoporous silica. A 2D-rectangular structure is identified as an intermediate structure between the 2D hexagonal and the lamellar structures. Moreover, the micellar structures are found to co-exist with the surfactant precipitates, which form a separate lamellar structure. The micellar structures are dependent on the NaOH concentration, surfactant concentration and the temperature. The effects of these three parameters are discussed. The result is also compared with the structures in the mesoporous silica system for a deeper understanding on the structure forming mechanism at different conditions.

4.3.1 The sample preparation and characterization

For obtaining a homogeneous mixture of the surfactant (received from Ajinomoto Co. Inc., purity 97%) and the solution, the weighted mixture was homogenized by centrifuging back and forth until it’s visually homogeneous, followed by stabilization at $80^0\text{C}$ for 5 days. The sample is further stabilized at room temperature for more than 2 weeks. Infrared (IR) spectroscopy was
Figure 4.1: The IR spectrum of the samples 60wt%-0.6mol/L (top) and 60wt%-
water(middle) in comparison with that of the original surfactant (bottom). All
three spectrum show a peak at 3310 cm\(^{-1}\), which corresponds to the stretching of
the secondary amine group, while if the amine group of the surfactant breaks to
form primary amine, a new peak at 3400 cm\(^{-1}\)-3500 cm\(^{-1}\) should appear.

performed to make sure no reaction has happened to the amine group of the sur-
factant molecules during homogenization process. For this the samples were
dried in vacuum for more than 3 hours before measurement to eliminate the
affection of water. The absorption curve obtained is compared with that of raw
surfactant to make sure no peaks corresponding to the primary amine (with
two modes of N-H stretches: asymmetrical N-H and symmetrical N-H stretch)
were observed. An example of the IR spectrum is shown in Fig.4.1.

Small angle X-ray scattering (SAXS) experiments with temperature con-
trolling attachment were performed on Nano-Max (RIGAKU Japan), with the
detectable \(q\) value ranging from 0.06 to 6 nm\(^{-1}\). A Pilatus 100K two dimen-
sional X-ray area detector (172um*172um pixel size with 487*195 pixels) was
used for detection. Each sample was sealed inside borosilicate glass capillary
with diameter of 1.0mm. The temperature was increased in rate of approx-
imately 10\(^{\circ}\)C/min. When the desired temperature was reached, the sample is
left for equilibrium at that temperature for 20min before the diffraction patterns
were collected. An exposure time of 5 min was chosen based on the highest
count of the peaks with sufficient signal-to-noise ratio. The temperatures of 30°C, 50°C, and 70°C were targeted for each sample. Strictly speaking, the structures at 50°C and 70°C are not necessarily equilibrium phase, since the 20min equilibrium time is chosen so that the structures can change back after a heating-cooling loop, which is a necessary but not sufficient condition for equilibrium. Still the we could discuss the temperature effect on the structures at each NaOH and surfactant concentration.

4.3.2 Results and Discussions

The co-existence of micelles and precipitate of surfactant $C_{14}GlutANa$

![Diffraction Patterns](image)

**Figure 4.2:** The indexes of the typical diffraction patterns of obtained structures. From top to bottom are lamellar (60wt%, water, 30°C), 2D-hexagonal (60wt%, 0.6mol/L NaOH, 50°C), 2D-rectangular (70wt%, 0.8mol/L NaOH, 30°C), Pm-3n (30wt%, 0.4mol/L NaOH, 30°C). The co-existing lamellar structures formed by surfactant precipitates are indicated by the arrows, which correspond to indices of 10 and 20 respectively.

At higher than 30wt% surfactant concentration, where surfactant liquid
crystals are formed, the X-ray diffraction pattern in most cases contain a lamellar phases with unit cell size of around 2.85 nm (Fig. 4.2). This size matches the length of our surfactant molecule composed of 14 carbon chain and a head-group, indicating a close contact of the surfactant molecules, i.e. lamellar structure of surfactant precipitates. Such precipitate structure prevails the conditions at 30°C and 50°C, and only disappear at 70°C for several NaOH and surfactant conditions.

**Structures in the phase diagram**

![3D phase diagram of the micellar structures](image)

**Figure 4.3:** The 3D phase diagram of the micellar structures expressed in the variables of surfactant concentration, NaOH concentration in solvent and temperature. The co-existence of the surfactant precipitates is also expressed in the diagram by the arrows.

If the peaks of the lamellar structure are excluded, the remaining set of peaks can be attributed to the micellar structures. The structures are determined from the XRD patterns by referring to the existing structures in the mesoporous silica counterpart [26] (Fig. 4.2). Among the identified structures are the Pm3n structure, 2D-hexagonal structure which are also found in the mesoporous silica materials. In addition, micellar lamellar structure is also found in the liquid crystal system. Moreover, a new structure is identified in the diagram, which are normally formed in vicinity of lamellar structure. The peaks can be indexed by assuming a 2D rectangular unit cell with unit cell size of around a=9.4nm, b=4.4nm. Derived from unit cell of the micellar lamellar structures (around 4.8nm) and that of 2D-hexagonal structures (around 4.8nm).
Figure 4.4: The phase diagram of the samples at 30°C.

The plane group is suspected to be $C2mm$, so that the micelles has an similar arrangement to that of 2D-hexagonal structure, with each micelles elongated to give the rectangular unit cell. A suspected structure transformation relationship is shown in Fig. 4.5.

Figure 4.5: The Schematic demonstration on the structure transformation from lamellar to 2D-rectangular and then to 2D-hexagonal structure.

The effect of NaOH concentration

The NaOH concentration dependence can be clearly visualized at 30°C and 30wt% surfactant. With solvent of water, no clear liquid crystalline phase can be distinguished from the random peaks at low q values. Increasing the NaOH concentration to 0.2 mol/L merges these peaks into one broad peak that corresponds to d spacing value of 4.9nm, and further a NaOH concentration above
0.4 mol/L leads to the structure that can be indexed by space group of \( Pm\bar{3}n \) (Fig. 4.2). The ionization of the surfactant headgroups is considered to be the reason of such structure change: from the irregular aggregate to a more monodispersed micellar structure and then to period liquid crystalline phase, the increase of NaOH increases the repulsive forces between surfactant headgroups by ionization of the carboxyl group, which introduces a thicker double layer between two ionized micelles that can prevent the micelles from unstable random merging. The balance of the repulsive electrostatic force and attractive van der Walls force thus stabilize the micellar structures. On the contrary, the lack of ionization leads to a thin double layer, increasing the possibility of random micellar reconfiguration, and thus a wider range of micelle size is formed.

The NaOH also plays the role of increasing the curvature of the micelles, shown at other surfactant concentrations and at 30\(^0\)C: At 60wt\%, the increase of NaOH has changed the lamellar micelle structure into the \( Pm\bar{3}n \) structure. At 70wt\%, 2D rectangular structure appears at 0.8mol/L NaOH after the lamellar structures at lower NaOH concentrations.

**The effect of temperature**

Considering the entropy of the surfactant tails, at higher temperature it would enriched the configurations of the surfactant tails, leading them to occupy a larger volume, thus a higher surfactant packing parameter \( g = V/a_0h \). The increased \( g \) parameter in turn leads to a decreased micellar curvature, that explains the micellar structure transformations in the system:

The \( Pm\bar{3}n \) structure at 60wt\% surfactant and 0.6mol/L NaOH transforms into 2D hexagonal structure when the temperature is increased from 30\(^0\)C to 50\(^0\)C. Similar transformation was found in the mesoporous counterpart, through a charge-density change during the silica condensation process. At different conditions, the structures being transformed are slightly different, like at 60wt\% surfactant and 0.2mol/L NaOH, the structures are transformed from \( Pm\bar{3}n \) to 2D rectangular structure instead of the 2D hexagonal, due to the lower ionization degree of the surfactant headgroup, as discussed above.

**The effect of surfactant concentration**

The surfactant concentration affects the packing of the micelles in an attempt to minimize the contact of the micelles’ surface. Higher surfactant concentration tends to arrange in micelles of lower curvature, since micelles are forced to come closer. This effect can also be nicely demonstrated at 30\(^0\)C (Fig. 4.4). In surfactant/water system, the structure transformation from micellar structures below 50wt\% into lamellar structures above that concentration, while
with 0.2mol/L NaOH, the structure is transformed into lamellar from $Pm\bar{3}n$ structure, similar to the case of 0.8mol/L NaOH, where $Pm\bar{3}n$ transform into lamellar through the intermediate 2D-Rectangular structure. All these transformations is towards a lower curvature with increasing surfactant concentrations.

4.4 A comparison between structures in mesoporous silica and liquid crystal

The structures of the liquid crystals have less diversity compared to that of the mesoporous silica, and also the transformation behaviour is different, as shown in the above example. Besides the kinetic feature of the mesoporous silica growth process that brings variable long-range configurations by assembling short-range units in different ways, just like the occurrence of the random and modulated tilings made from squares and triangles [74], other parameters should also be involved to explain the diversified periodic lattice types. Some consideration based on the observed results are discussed below for the $C_{14}GlutANa$ surfactant, as well as the $C_{14}S$ surfactant that produces the tricontinuous mesoporous silica for the first time.

4.4.1 The $C_{14}GlutANa$ system

To consider the stabilization mechanism of various structures in soft micellar system, the elucidation of geometric principles is considered to be more important than detailed quantitative analysis based on models that - owing to the intricacies of the physical system - incorporate many parameters, few of which can be measured directly [60]. The discussion below thus compares the geometries obtained in liquid crystal and mesoporous silica, and tries to extract the geometry principles that differentiate those structures in stabilization under specific conditions.

Comparison on ”cage type” structures

One feature in the liquid crystal is the prevailing $Pm\bar{3}n$ structure (Fig. 4.3), while in mesoporous silica several more structures were obtained adjacent to it, like $P4_2/mnm$, $Fd\bar{3}m$ and $Fm\bar{3}m$ [26]. All these structures are “cage-type” and have the similar $g$ parameter of around 1/3 [35], thus the curvature does not contribute much in differentiating such structures. One important characteristic of $Pm\bar{3}n$ structure is that it’s the up-to-now best candidate in surface minimization with respect to Kelvin’s problem: what space-filling arrangement of cells of equal volume has minimum surface area? Such characteristic differentiates $Pm\bar{3}n$ structure from others. A comparison of the surface areas among
the Tetrahedrally Close-Packed Structures \textit{Pm\bar{3}n}, \textit{P4_2/mnm} and \textit{Fd\bar{3}m} were done \cite{43}, where both \textit{Pm\bar{3}n}, \textit{P4_2/mnm} are shown to have smaller surface area compared to Kelvin’s original proposal of BCC structure, while \textit{Fd\bar{3}m} gives larger value than BCC. Still, \textit{Pm\bar{3}n} leads the optimum result among them. This fact indicates that the surface minimization is the leading parameter that stabilizes the liquid crystal, so that other structures inferior in this aspect were excluded from existence in the system.

The existence of other structures with less surface-minimization features in mesoporous silica is partly related to the introduction of the CSDA, which brings more flexibility to the base surfactant molecules. The \textit{Fd\bar{3}m} structure, for example, is composed of two kinds of cages: 5\textsuperscript{12}6\textsuperscript{4} and 5\textsuperscript{12}, whose size difference is comparatively larger than that of \textit{Pm\bar{3}n} composed of cages of 5\textsuperscript{12}6\textsuperscript{2} and 5\textsuperscript{12}. This is facilitated by a larger CSDA/surfactant molar ratio in synthesizing the \textit{Fd\bar{3}m} structure (7 \geq \text{CSDA/}C_{14}\text{GluA} \geq 2) compared to that of \textit{Pm\bar{3}n} (\text{CSDA/}C_{14}\text{GluA} \leq 2). The \textit{Fm\bar{3}m} in the mesoporous silica material on the other hand brings the consideration of close packing of spherical micelles. A pre-requirement of the spherical micelles is made possible by the high CSDA that covers the surfactant micelles, while the high NaOH concentration accelerate the consolidation of such CSDA layer to form a relatively hard consolidated silica shell before completion of the self-assembly of the surfactant micelles, preventing the surfactant molecule to exchange between micelles. Thus a hard sphere packing phenomenon is initialized to produce such close-packed structure. The repulsion between micelles induced by the ionized surfactant head group is not enough to form such “hard” spheres so that a surface-minimization mechanism takes over, which explains the formation of \textit{Pm\bar{3}n} at lower CSDA concentration in mesoporous silica and also the exclusivity of such structure in liquid crystal.

A comparison between 2D rectangular structure to \textit{Pn\bar{3}m}

In mesoporous silica, when the ionization degree is lowered from the structure of \textit{P6mm}, the bi-continuous structure of \textit{Pn\bar{3}m} is formed. However, such structure was not found in the liquid crystal. Instead, an intermediate 2D rectangular structure is formed in between the 2D hexagonal and lamellar structures. Since both structures have intermediate curvatures between 2D hexagonal and lamellar structure, the curvature should not be the factor that differentiate them. Remember that the \textit{Pn\bar{3}m} structure is a counterpart to the triply periodic minimal surface D, which is quite often compared to another ubiquitous minimal surface G. These two surfaces are identical in terms of local surface curvatures, but different in the global homogeneity \cite{60}, which is described by the area weighted distance deviation between the actual surface and the medial
surface. Such distance deviation in principle can be minimized to zero by the 2D rectangular structures, as shown in Fig. 4.5, thus it superiors to the $Pn\bar{3}m$ structure in this aspect. In the mesoporous silica case, on the other hand, the flexibility enhanced by the CSDA allows a wider range of distance distribution and thus $Pn\bar{3}m$ is favoured due to its low curvature deviation [51].

4.4.2 The $S_2C_{14}$ system

A short background of tri-continuous structure

A mathematically predicted tri-continuous structure was for the first time synthesized in mesoporous silica material [31]. The structure is formed in between the 2D hexagonal structure and the bi-continuous structure of $Ia\bar{3}d$. Although efforts have been done on obtaining the same tri-continuous structure in other system where 2D hexagonal and bi-continuous structures were previously obtained, the quality is not comparable to the original synthesis and is quite sensitive to the environmental conditions [78]. The special surfactant of (S)-(1-tetradecylcarbamoyl-2-phenylethyl)-dimethylethylammonium bromide ($S_2C_{14}$) used in the original synthesis should be the major factor that direct to such unusual structure. In the original synthesis [31], the forming mechanism is discussed from the curvature aspect, concluding that the tri-continuous structure is formed as its curvature distribution is in between that of the 2D hexagonal and $Ia\bar{3}d$ structure. Geometrical consideration of several polycontinuous geometries is done afterwards [59], showing the possibility of forming such multi-interwoven structures with similar molecular architectures that are used for obtaining novel bi-continuous structures. In this work, a trial is done to investigate the liquid crystalline structures using the same surfactant of $S_2C_{14}$, to study the structure behaviour in a thermodynamically stable environment. The preparation method is similar to that of $C_{14}GlutANa$ described above so that the contents below will focus on the results. A comparison of the $Ia\bar{3}d$ and tri-continuous structure models are performed afterwords in an attempt to understand more of such special structure.

The liquid crystal structures of surfactant $S_2C_{14}$

The $S_2C_{14}$ surfactant shows an unstable feature at lower than 70wt% surfactant concentration, as when the temperature is increased from room temperature, additional peaks appear at low q values, which are not indexable (Fig. 4.6). Thus the structure investigation is constrained under room temperature.

From the XRD patterns, we could see that $Ia\bar{3}d$ structure is formed directly after the non-periodic micellar phases (Fig. 4.7). And the $Ia\bar{3}d$ structure covers a wide range of surfactant concentration range, i.e. from ~ 50wt% to 70wt%.
**Figure 4.6:** The XRD patterns of the sample with 60wt% $S_2C_{14}$ surfactant at different temperatures. Random peaks at low q values appear at higher than 300°C which is not indexable.

Although small concentration change was done in between the non-periodic micellar and the $Ia\bar{3}d$ structures, 2D hexagonal structure still could not form, which indicate that the intrinsic architecture of such surfactant adopts a high g value, and could only lead to structures with low curvatures, such as bi-continuous and possibly lamellar structure.

The less diversity in the liquid crystal compared to that of the mesoporous silica in the $S_2C_{14}$ surfactant system can be understood considering the properties of the $S_2C_{14}$ surfactant molecule: unlike the case of $C_{14}GlutANa$, the PH change, which induces the structure change of mesoporous structures, does not act on the $S_2C_{14}$ surfactant, since its head group is already salt and does not change with PH value. Instead, as discussed in the original article [31], the PH value acts on the silica species to change their charge density. A charge-matching between the surfactant and the silica species leads to the different
The XRD patterns of the samples at room temperature, with surfactant concentration ranging from 40wt% to 70wt%. Below 50wt% the XRD patterns indicate non-periodic micellar structures, while from 52wt% the structure of \( Ia\bar{3}d \) starts to form. Until 70wt% the peaks can be indexed by the same space groups of \( Ia\bar{3}d \) structures with different curvatures, resulting in the tri-continuous structure. The liquid crystal system does not contain components that can work the similar way as the silica species, and thus can only adopt the structure according to the intrinsic surfactant molecule architecture, affected only by the surfactant concentration and the temperature. As higher temperature normally decreases the curvature of the micelles due to the increased entropy of the surfactant.
tails, it's unlikely the \( Ia\bar{3}d \) structure formed at room temperature will transform to tri-continuous structure with increasing temperature. Moreover, the peaks formed at higher temperature indicates reaction may happen at higher temperature, which makes the discussion on the structure forming mechanism difficult.

The distance deviation comparison between tri-continuous and G surfaces in mesoporous silica

In the original work, the curvature distributions of the three structures: 2D hexagonal, tri-continuous and \( Ia\bar{3}d \) are compared. Although in average the curvature decreases from 2D hexagonal to tri-continuous and then to \( Ia\bar{3}d \), the deviation of the curvatures is largest for the tri-continuous structure. This large span of the curvature distribution is not favoured when we consider the Helfrich energy \[51\]. It is thus suspected whether the global homogeneity can be better for such structure to compensate the flaw in Helfrich energy, in an attempt to explain the stabilization of tri-continuous structure. \[60\]. The comparison of the global homogeneity on the structure models of IBN-6 (\( Ia\bar{3}d \)) and IBN-9 (tri-continuous) is thus done.

The structure factor data in the original work is used to reconstruct the electron density map of both IBN-6 and IBN-9 and the threshold is determined using the gas adsorption data also from the original work. The interfaces between the silica wall and the pore channel are extracted from the reconstructed structure model. Random meshes are drawn on the surfaces. To make sure each vertex of the mesh represent a similar area on the surface, a denser mesh set is first performed on the surface, followed by a process that removes the adjacent vertices with distance smaller than \( r \), so that for a surface patch of area \( \pi r^2 \) there is only one vertex in it. In this way the count on the vertex number of the meshes can be directly related to the surface area. The number of vertices on the surface is increased until the final result converges, and finally a set of more than 2000 vertices are drawn on the asymmetric unit of one unit cell for both structures.

The medial surface- actual surface distance distributions are obtained for both structures and are shown in Fig. 4.8. From the figure we could see that for both structures, the distance distributions are concentrated on one value around 1.7 nm, and the homogeneity of IBN-9 material is even slightly worse than that of IBN-6, which means the tri-continuous structure does not surpass the bi-continuous structure either in terms of global homogeneity nor the Helfrich energy. The intermediate averaged curvature is thus still the only explanation for its stabilization. Further work may be considered on the chirality of the surfactant molecules, which may affect the chirality features of the meso-
Figure 4.8: The medial surfaces of (a) the IBN-6 structure and (b) the IBN-9 structure obtained from their structure models. The distance distribution are shown on the right respectively. The vertex number for structure model (a) and (b) are 5494 and 8468 respectively, so that for each case the asymmetric unit has more than 2000 vertices.
5. The application of Low-Voltage HRSEM to various materials

The possibilities with SEM is largely extended when Low voltage is achieved together with the maintained high resolution, by either a energy-coherence-enhanced electron gun or a “Gentle beam” design where the high voltage electron beam is decelerated above the sample holder. These possibilities include 1) the true surface information that comes from the shallow interaction volume, 2) the eliminating of charging problem when critical energy is reached at \( \lesssim 1 \text{keV} \) incident energy, 3) the ability to finely tune the SE yield to enhance the contrast between non-conductive materials of similar components, 4) the reduction of the damage to the beam sensitive materials, and probably more. In this chapter I would like to introduce some applications of HRSEM in my thesis work to various materials that can hopefully guide future work on this widely used and easy-to-handle instrument, especially on the low voltage range, the theories involved were mainly described in Section 1.2.1.

5.1 Voltage variation around critical energy

From Fig. 1.6 we could see that the low accelerating voltage could solve the charging problem quite well, if the accelerating voltage can be lowered to the critical energy, so that there is no accumulation of electrons in the sample irrespective of its conductivity property. The ability to reduce the charging problem has successfully brought the SEM into a novel characterization method for porous materials, which are quite often insulating but requires high resolution. By combination with the cross section polisher, it has become possible to get a 3D view of the porous structures, which were previously only possible under TEM. In Fig. 5.1 we could see a cross section of the mesoporous silica with space group of \( \text{Im} \bar{3}m \), the pores are clearly visualized and the sharp FFT diagrams make a direct indexing possible.

In addition to the ability in solving charging problem, for two or more materials with similar components, the different energy dependence curves
can be utilized to enhance the contrast between them. The concept can be easily understood by the graph in Fig. 5.2 where the SE yield curves of two materials A and B are shown. At the energy where the two curves cross, the $\delta$ value is the same thus these two materials have no contrast between each other. An energy lower than this value leads to a higher SE yield for sample B compared to A, thus B would look brighter in SEM images, while higher energy reverses the contrast due to a higher $\delta$ for sample A.

An example can be shown on two components with close atomic numbers: $SiO_2$ and C. The $SiO_2$ is considered as insulator and thus is suffering from charging problem under SEM at conventional accelerating voltages, while C is a nice conductor and is quite often used as sample substrate to help reduce the charging problem. The contrast difference of these two materials is quite large under conventional accelerating voltage (e.g. 5kV) due to their different electric conductivity properties (Fig. 5.3). However, when the voltage is decreased, the contrast is governed by the SE yield instead of the conductivity. As can be seen from Fig 5.2, it is possible that the $SiO_2$ got lower SE yield than C if the energy can be finely tuned. With the help of Low voltage SEM, this phenomenon can be experimentally proved. A series of the images under different accelerating voltages were taken for the mesoporous silica ($SiO_2$) on graphite substrate (C). From 0.5kV to 1.7kV, the contrast between the silica and the graphite reversed, i.e. the silica appears darker at 0.5kV than graphite in the image, while their brightness more or less equals at 1.5kV, and when 1.7kV is applied, the silica shines more than the graphite substrate. The phenomenon fits well with the theory depicted in Fig. 5.2 and in this specific case the cross over of the two curves should corresponds to 1.5kV, with A

Figure 5.1: SEM image on the cross section of Mesoporous silica SBA-16. The left image has a “quasi-four-fold” symmetry, while the right is very close to a six fold symmetry. Boundary or defects exist between these two regions because of the change of the symmetry in this cross section.
representing carbon and B representing silica.

![Graph showing energy dependence of SE yield](image)

**Figure 5.2:** A representative energy dependence of SE yield for two kinds of materials with different components.

![Mesoporous silica SBA-16 and reciprocal carbon analogue FDU-16 images](image)

**Figure 5.3:** The Mesoporous silica SBA-16 (second row) and reciprocal carbon analogue FDU-16 (third row), both on graphite substrate, imaged at different accelerating voltages. Contrast normalized to that of the highly ordered pyrolytic graphite substrate. No stage bias. In-lens detector, Sb mode. Contrast along the lines drawn across the silica particles are shown on top, with the two sharp peaks in each image corresponding to the surface tilt contrast unrelated to the composition. . [66]
5.2 Combination of Low- and High- voltage for complete information

At high voltage, the interaction volume is large, which means the detected signals are from not only the surface bombarded by the electron beam, but also inside the sample bulk. This feature can be a bonus or disadvantage depending on the purpose of the characterization. A nice example is gold nano particles encapsulated by the Titania hollow spheres (Fig. 5.4). A lower accelerating energy enriches the surface topography information, however the lack of contrast between TiO$_2$ and Au makes it hard to distinguish them. Higher accelerating energy magnifies the Z contrast of different elements so that gold nano-particles can brighten out from the background of TiO$_2$. However with the larger interaction volume it becomes difficult to locate the depth of the particle. Thus a combination of low and high accelerating energy is always desirable for a complicate characterization of the specific materials.

![Image of HRSEM images taken at different landing energies](image)

**Figure 5.4:** The HRSEM images taken at different landing energies where (a, b) a reduced landing energy (500v) clearly shows the topographic information of the encapsulated gold while a higher landing energy of 3.0 kV (c) gives enhanced contrast of gold particle. [66]

5.3 Z and topographic contrast at low voltage

Due to the diminish of the BE, normally at low voltage it is considered that the Z contrast will be lost and one could only obtain topographic information. From the paragraphs above we could see that one still see the contrast of different components if the energy is tuned properly. Another factor that hampers the observation of the Z contrast is the sensitive tilt contrast from the SE, as described in Fig. [1.5] and can also be seen from the bright contrast on the edges of the particles in Fig. 5.3. Thus in order to get a clear Z contrast in low voltage, a flat surface is highly desired.
For printing paper, it’s necessary to observe the cross section of the pigment layer in order to get a statistic understanding on the paper’s content distribution, which could facilitate a economic and environmentally friendly design of the manufacturing procedure. However, due to the charging problem, the paper was for a long time studied by pre-treatment such as stain or coating, which could introduce distortion to the original state of the paper. Now the charging problem can be largely eliminated by applying low voltage electrons, with which comes another problem of contrast: Since the pigment (calcium carbonate) and their bonder latex have similar components, to distinguish them is difficult under a rough cross section. A flat cross section could make it possible to discern the pores, latex and pigments. For this an ion polished sample could meet the requirement, with a flat surface gently polished by ion with minimum destruction on the cross section. With such flat and pristine cross section, we could see clearly the contrast between the pigments and their binder latex by tuning the accelerating voltage of the SEM. A statistical image analysis is thus possible on the cross section of the papers for a unprecedentedly accurate result (Fig. 5.5).

Figure 5.5: The SEM image of the cross section polished by CP (left), with the voids, pigment particles and latex binders easily distinguished by their difference in contrast and their proportion in the paper coating part can be calculated by counting each content’s area as shown in the right figure. [67]

The sensitivity of the SE can also give nano-scale information on the topographic information of flat cross sections, which were previously only possible under atomic force microscope (AFM). This property has been successfully applied to the surface characterization of the microporous crystals to investigate the crystal growth process [66], as the fingerprint of the growth process can be nicely visualized by SEM with similar resolution compared to that of AFM. The significance of the sensitivity of SE compared to that of BSE was interestingly demonstrated in the cross section of Yttria stabilized zirconia material, where stress could induce a phase transformation from tetragonal to monoclinic structure, accompanying a ≈ 3% increase in volume. This trans-
formation quite often happens on the surface and has been tested using x-ray photoelectron spectroscopy due to the coordination difference of the Zr in the two different phases [13]. However, the surface protuberance due to the minor volume change is so small to be seen even with a flat surface, which is largely due to the comparatively large interaction volume, from which the generated signals greatly surpassed the single from surface. A separation of the SE from a mixed signals of SE and BSE thus helps to enhance such surface signal.

In our recent observation, the in-lens detector has successfully revealed the nano-meter surface roughness of Yttria stabilized zirconia prepared by laser sintering method. A comparison of the images taken using the in-lense and the Everhart Thornley detectors (Fig. [1.7]) can be seen in Fig. [5.6]. Under the same beam condition, the images obtained using different detectors show completely different contrast, revealing the surface (using in lens-detector) and crystalline orientation (using Everhart Thornley detector) information respectively.

**Figure 5.6:** The images of the cross section of Yttria stabilized zirconia taken by the Everhart Thornley detector(left) and the in-lens detector(right) respectively. The contrast in the left image is from the orientation difference of different crystalline domains, while the completely unrelated contrast shows the tiny surface protrusions that are not visible on the left. (sample by courtesy of Bin Qian)
Knowing the structures of the mesoporous silica and understanding the mechanism that leads to such structures are complementary to each other: to understand the forming mechanism needs a detailed structure information, while the structure-forming process can be better controlled if the mechanism is clearly understood. In this thesis, the structures of the mesoporous silica crystals are investigated, mainly using an electron microscopy approach. Based on the structure models established form the electron microscope images, the growth mechanism was proposed and modelled to compare with the experimental results. Both the revealed structure information and the accordingly proposed mechanism could aid a further development of such materials.

In synthesising the mesoporous structures using an anionic surfactant, a quasicrystalline structure was obtained together with its periodic approximant structures. The 2D tiling features of the 3D structures were studied using a phason strain approach for clarifying its quasiperiodicity. All such revealed structure details help abstract a theoretical model that matches well with the experimental result. Assuming a kinetic crystal growth process, the mechanism that affects the formation of the aperiodic structures is proposed. The generality of such mechanism may aid not only the further development of mesoporous silica but can be expanded to other soft-matter systems.

From a similar anionic surfactant, the interesting structure transformation is triggered by introducing swelling agent TMB in the synthesis. Such transformation mimics the minimal surface transformation from G to D, whose difference in terms of stabilization mechanism is still under research. Together with an attempt to model the structure details from TEM images, the kinetic study was performed to follow the structure evolution during synthesis and hydrothermal treatment. From the TEM study, an epitaxial relationship between the two structures is discovered. The kinetic study revealed that the silica hydrolysis and condensation also play a role in affecting the structure transformation in addition to the introduction of TMB. In this study, different approaches used in the reconstruction process were attempted and their constrains are discussed respectively.

To obtain a thermodynamic basis for considering the micelle-templated crystal growth, the liquid crystal structures of the surfactant-water(NaOH solution) systems were investigated. For the anionic surfactant $C_{14}GlutANa$, the
structures of 2D hexagonal, \textit{Pm\textbar{3}n}, lamellar are obtained, together with a new 2D rectangular structure as an intermediate structure between lamellar and 2D hexagonal structures. The stabilization mechanism of these structures were discussed in comparison with the structures formed in mesoporous silica system. Moreover, a co-existence of the surfactant precipitates with the micellar structures are discovered in this surfactant system, raising the concern on its Krafft temperature. Another trial on liquid crystal structures were done on the \textit{S}_2\textit{C}14 surfactant that was used to produced a tri-continuous mesoporous silica structure. The prevailing \textit{Ia\textbar{3}d} structure found in the liquid crystal has shown the importance of the silica species in affecting the ultimate structures of the mesoporous silica in addition to the surfactant template.

Electron microscopy is utilized to great extent in the thesis work, together with sample preparation techniques using ion beam. The advantages of low-voltage SEM was especially explored in my study, with important information revealed from several materials, which could not be done using conventional voltages. Several examples during my study are demonstrated to help a better interpretation of the contrast in the SEM images and aid other researchers in exploring the possibilities of SEM. These examples also shows a part of the future prospects on scientific studies offered by such technical improvements.
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References


