AGGREGATION PHENOMENA IN PARAFFIN MIXTURES

DEDICATION

A thesis submitted for the degree of Doctor of Philosophy at
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by

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DEDICATION

To my parents

献给我的父母亲
PREFACE

This thesis contains no material previously submitted for a degree in any other University. The cooperation has been maintained throughout with my supervisor, Professor J. W. White.

Peng Wei Zhu
I would like to express my sincere thanks to my supervisor, Professor J.W. White, for his outstanding guidance, continual encouragement, and much-needed help throughout the course of this work. The many fruitful discussions and challenging ideas are highly appreciated. His kindness and great patience in correcting the English of this thesis have made my writing more enjoyable and an unforgettable experience.

I am very grateful to all the members, both the past and present of Professor White’s research group, for their help and friendship.

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I am very grateful to Mr. Graham Lindsell and Dr. Vittorio Luca for the helpful proofreading of Chapters 3 and 6 of this thesis, respectively.

The receipt of an Australian National University Ph.D. Scholarship is gratefully acknowledged.

Finally, and very importantly, a special thank-you for my wife, Mi Feng, for her selflessness and understanding during my studies.
SUMMARY

In this thesis, paraffin mixtures have been investigated as models to represent more complicated systems. The studies focus primarily on the microphase separation and its dynamics in paraffin mixtures, and aggregation phenomena in mixtures of paraffins and a polymer.

The study of the dynamics of phase separation in condensed matter is not only important for material applications but of uttermost significance for our understanding of nonequilibrium patterns and the evolution of order in systems far from thermodynamics. We here have systematically investigated the kinetics of the demixing processes in binary mixtures $C_{30}H_{62}/C_{36}D_{74}$ and $C_{30}D_{62}/C_{36}H_{74}$ by using small angle neutron scattering (SANS). The results are discussed in terms of modern theories of dynamics. It has been found that the dynamics at later stages can be described by existing scaling functions. The results suggest that vacancies or conformational defects play a role in the demixing processes.

We have studied the structural arrangement of two components as well as the morphological transition between commensurate and incommensurate solids in $C_{30}H_{62}/C_{36}D_{74}$ system. The equilibrium structure has been described by one dimensional correlation function and the paracrystalline model. The interfaces of separated lamellae was also studied.

The study was extended to binary paraffin solid solutions by means of the small angle x-ray scattering (SAXS). The results are of interest in connection with effects of the temperature and composition on the integrated intensity, the microstrain, the paracrystalline distortion, and over-all interfacial thickness between lamellae.

A new correlation function was presented to describe the essential features of aggregate structure by considering effects of partial ordering and deviation from Porod’s law. The new scattering formula has been applied to mixtures of paraffins and polydimethylsiloxane (PDMS). Because the new model includes features of existing ones, it can be easily extended to systems with similar scattering patterns.
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CHAPTER ONE  INTRODUCTION

In this thesis, paraffin mixtures are investigated as models to represent more complicated systems. The studies focus primarily on the aggregation phenomena in paraffin mixtures and mixtures of paraffins and a polymer.

1.1 PARAFFINS

Since paraffin mixtures and other properties in mixtures containing paraffins involve characteristics of pure aliphatics, an understanding of pure paraffins is necessary.

In an excellent review article [1], Mnyukh summarized and discussed most of the early experimental data on the structure of normal paraffins and their solid solutions. Beginning with the classic studies of Muller [2-3], the various crystal modifications of paraffins have been found and studied in detail. The behavior of solid-solid transitions has been extensively reported. At low temperature, several modifications [4-6] occur depending on the chain length. These modifications are associated with closely packed arrangements of extended molecular chains. As the temperature increases, orthorhombic paraffin crystals tend toward hexagonal symmetry [3] which was first observed by Muller. He also proposed [3] that in the hexagonal phase, molecules rotate as rigid rods around their long axes and therefore the name of rotator phase for disordered crystal was given. The rotator phases usually form when the temperature approaches the melting point. In the rotator phases, paraffin chains are tilted with respect to the molecular layer normal. In the most cases, solid-solid phase transitions, i.e., transitions between different modifications, are of the first order and accompanied by the introduction of defects. In what follows, the current investigations on paraffins are briefly reviewed by referring the experimental results which are believed to be of basic importance.

Recently, knowledge of the structure and behavior of solid-solid transitions in paraffins
has been improved very much due to higher resolution diffraction techniques. Some of the studies are those of Dorset and co-workers[7-12], who analyzed the crystal structures of samples epitaxially crystallized on benzoic acid by using electron diffraction. The $0kl$ diffraction patterns obtained from the even-numbered paraffins in the range from $C_{32}H_{66}$ to $C_{60}H_{122}$ prepared in this way indicate that all these paraffins pack in the orthorhombic unit cell, in agreement with the earlier x-ray analysis. The three dimensional analysis for the odd-numbered paraffin $C_{33}H_{68}$ has found that the crystal structure is orthorhombic rather than the twinned monoclinic reported earlier. Dorset's work also extended to the rotator phase. The changes in electron diffraction patterns obtained from epitaxially crystallized $C_{36}H_{74}$ crystals have been interpreted as the contributions from irregular chain end packing between lamellae. The solid-solid transition was found to be reversible.

Spectroscopic studies of the distribution of conformational disorders and the phase transition have been excellently carried out in Snyder's group[13-15] by selective deuteration. They viewed molecules as rigid all-trans conformers displaying rotational and translational motions. In a subsequent study[16], it was found that: (a) detectable defects are formed in the rotator phase, and conformational defects present in the rotator phase are end-gauche, double gauche, and kinks; (b) the distribution of the defect concentration along the chain itself is not uniform. The highest concentration of defects is at the chain end regions. The concentration of defects decreases exponentially in going toward the middle of chains; (c) the concentration of defects at a specific carbon position on the chain increase with increasing chain length; and (d) the concentration of defects at a specific carbon position on the chain is strongly the temperature dependent. The Dill-Flory model has been modified for application to paraffins[16].

By using small angle x-ray scattering(SAXS), Strobl et al[17] investigated the longitudinally molecular motion and intramolecular conformational defects in $C_{33}H_{68}$, where four crystal modifications were found and studied in detail. The defect structures in paraffin crystals can be divided into three classes: orientational disorder, longitudinal disorder and intrachain defects. The existence and magnitude of these types of disorder can be established from a set of structural parameters related to the intensity and position of the small angle $00l$ reflections of powder diffraction patterns. Similar studies on odd-numbered paraffins in the range from $C_{19}H_{40}$ to $C_{27}H_{56}$ were carried out by Craievich et
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al[18]. The conclusions drawn from their results are that: (a) defect structures are mainly present at higher temperatures, i.e., at rotator phase; (b) longitudinal molecular motion dramatically increases at the temperature of solid-solid transition and the magnitude of this motion increases with increasing temperature; (c) the longitudinal disorder in paraffins increases with increasing chain length; and (d) the concentration of intramolecular defects is a linear function of molecular length and a minimum chain length is required for the formation of kinks.

A series of x-ray and differential scanning calorimetry studies of the rotator phase for odd-numbered and even-numbered paraffins was carried out by Doucet and co-workers[19-22]. For odd-numbered paraffins, the rotator phase in C_{17}H_{36}, C_{19}H_{40} and C_{21}H_{44} has a base-centered orthorhombic unit cell, space group Ccmm, in C_{23}H_{48} and C_{25}H_{52}, the orthorhombic unit cell transforms into a hexagonal modification of undetermined structure a couple of degrees below the melting point. For even-numbered paraffins in the range from C_{18}H_{38} to C_{26}H_{54}, the rotator phase is characterized by a bilayer packing with molecular axes perpendicular to the layer planes and within each layer the packing is hexagonal. Unger[23] studied paraffins with carbon number ranging from 11 to 25. His results concerning the shorter molecules of paraffins indicate that with increasing temperature, paraffins undergo a first order transition into an orthorhombic phase with an F-centered unit cell and not C-centered as proposed before. This result also modifies the conclusions concerning the intralayer packing and molecular disorder. Zerbi et al [24] have also reported on gauche-bond concentration at the chain ends and at the chain middle for paraffin C_{19}H_{40}. They did not observe gauche bonds in the chain interior. Incoherent neutron scattering has been used to describe molecular motions of paraffins in the rotator phases[25-30]. The orders of magnitude of rotator and translation diffusions have been determined for some paraffins.

Very recently, Basson and Reynhardt[31] have reported motions of defect chains at the low temperature phase by using nuclear magnetic resonance(NMR). The mechanism of molecular motions was proposed. The results indicate that the gauche defect equilibrium orientation has a higher energy than that of the ordered all-trans equilibrium orientation. The energy difference between the all-trans and the gauche orientation is estimated to be in the range 10-14 (kJ/mol) and seems to decrease with an increase in chain length.
On the other hand, computer simulations on the dynamics of paraffin chains have been performed in recent years\[32-36\]. The techniques of molecular dynamics and Monte Carlo calculation have been extended to the solid paraffins, both in the ordered crystalline phase and in the disordered rotator phase.

### 1.2 Binary Paraffin Solid Solutions

Many binary paraffin solid solutions have been studied, mainly by using powder x-ray diffraction and calorimetry techniques, as reviewed by Mnyukh\[1\]. These studies have shown that in the liquid state, paraffin mixtures with different chain lengths are fully miscible, but in solid phases the miscibility is strongly influenced by chain length difference and odd/even carbon number effects. Binary paraffin solid solutions often assume untilted structures even when the pure components are tilted. Kitaigorodskii et al\[37\] proposed rules which govern the formation of the stable solid solutions with different chain lengths and crystal structures of pure species. By using the Bragg-Williams approximation, Matheson and Smith\[38\] were able to formulate a simple scheme which can successfully predict which pairs of paraffins would form a series of solid solutions. Dorset\[39\] reported a more detailed map indicating which binary paraffin mixtures are miscible and which are not.

Recently, binary paraffin solid solutions have been studied in more depth. Dorset\[39-43\] successfully investigated a series of paraffin pairs by using electron diffraction and high resolution, low dose electron microscopy. Three types of solid state structure have been investigated: solid solutions, fractionated solid solutions, and the eutectic structure. The solid solutions and eutectic structure have been very well explained by Raoult's law, and Schroder and Lee's equations. The microphase separation has been found where a metastable solid solution crystallized from the melt slowly fractionated after several day ageing. Microphase separation in binary paraffin mixtures was first reported by Mazee\[44\] in 1958. He found that freshly melt-crystallized $\text{C}_{30}\text{H}_{62}/\text{C}_{35}\text{H}_{72}$ was initially a solid solution, but after a number of months had undergone some demixing. However, little attention on this phenomenon was received until Dorset recently reported\[39,41\]. Of particular relevance to this thesis, the fractionation in $\text{C}_{30}\text{H}_{62}/\text{C}_{35}\text{H}_{72}$ was found when the
sample was slowly crystallized from the melt and equilibrated for about 2 days at room temperature. The analysis of \( \text{C}_{30} \text{H}_{62}/\text{C}_{38} \text{H}_{74} \) structure from electron diffraction data indicates that the fractionated solid is a random sequence of pure paraffin lamellae with an exact match of methyl end planes occurring at lamellar boundaries. Dorset[45] also extended the study to solid solutions composed of perdeuterated paraffins and their hydrogenated analogous with identical chain lengths. The perdeuterated paraffins were found to have quite similar structure properties to paraffins with equal chain length. Binary phase diagrams were reported to be ideal for the phase boundary between the rotator phase and the melt, and for the orthorhombic to rotator transition.

Binary paraffin solid solutions have been studied in Snyder's group[46-47] by using vibrational spectroscopy and calorimetry techniques. They were concerned about the conformational disorder associated with each of two paraffin components for \( \text{C}_{19}/\text{C}_{21} \) and \( \text{C}_{49}/\text{C}_{50} \) mixtures. They found that the concentration of end-gauche defects is higher in binary mixtures than in pure paraffins. Conformational disorder induced by mixing was found in the region nearest ends of chains and chain interior was relatively unaffected. The concentration of end-gauche defects in longer chains of mixtures decreases with increasing the fraction of longer component. The occurrence of conformational disorder in a binary mixture is primarily determined by chain length mismatch rather than the average chain length. Snyder et al[48-49] have extended their work to the microphase separation in binary paraffin mixtures by using infrared spectroscopy. Very recently, they[49] reported the kinetic of microphase separation for the mixtures \( \text{C}_{28} \text{H}_{58}/\text{C}_{36} \text{D}_{74} \), \( \text{C}_{29} \text{H}_{60}/\text{C}_{36} \text{D}_{74} \), and \( \text{C}_{30} \text{H}_{62}/\text{C}_{36} \text{D}_{74} \).

Denicolo et al[50] studied the \( \text{C}_{23} \text{H}_{48}/\text{C}_{24} \text{H}_{50} \) mixture. Their results concerning the shorter molecules have identified all phases existing in this pair. Four stable solid phases were found. The observed phases are solid solutions of terminal phases. At lower temperatures, two ordered solutions with structures corresponding to those of pure components were detected. At higher temperatures, two disordered rotor phases exist. Two crystalline phases can coexist in a limited region at lower temperatures. The hexagonal phases of \( \text{C}_{23} \text{H}_{48} \) and \( \text{C}_{24} \text{H}_{50} \) have the same nature.

The phenomena of long range intermixing of binary paraffins were reported by Ungar
and Keller[51]. At a temperature below the melting point and even below the hexagonal phase transition, paraffin molecules were found to intermix when separate macroscopic crystals were pressed together in contact. This important discovery implies that paraffin chains have much greater mobility in the solid state than normally envisaged. Ungar[52] also initially investigated binary paraffins crystallized in a different orthorhombic modification. The change in structure was regarded as one of the reasons why there is unusually large depression of the rotator transition temperature upon admixture of another paraffin of slightly different chain length.

The melting of a number of binary paraffins was investigated by Bonsor and Bloor[53]. A value for the interfacial surface free energy lateral to the chain direction $\sigma_n$ of 3 erg/cm$^2$ was obtained and found to give good fits to the near equilibrium freezing of binary paraffins. An equilibrium density of vacancies in binary paraffins which accord well with the experimentally observed behavior of the solid state phase transition was calculated by using $\sigma_n$. The distribution of free energy between the crystallization and the remelting processes was estimated for $C_{19}H_{40}/C_{44}H_{90}$. It was suggested that a paraffin with half the lamellar spacing of a second paraffin may be stabilized in a solid solution of the longer with two of the shorter molecules aligning along one longer molecule in a lamella.

Very recently, new phase behavior in binary paraffin solid solutions was discovered by Sirota et al[54]. A set of new phase phenomena was found between the hexagonal and orthorhombic phases. The existence of restacking transitions has been identified within hexagonal rotator phase.

Basson and Reynhardt[55] have reported motions of defect chains at the low temperature orthorhombic phase by using nuclear magnetic resonance. The mechanism of molecular motions was proposed. The first motion is an end-gauche defect motion of longer chains while the second motion is a twofold screw motion of shorter chains. The vacancies created by the chain length mismatch lower the energy difference between the all-trans and gauche orientation. The probability that a shorter chain will be in the translational screw position depends on the composition of the sample and the temperature.
Chapter 1 Introduction

White et al.[56-57] have successfully investigated the phenomenon of the microphase separation in a $C_{30}H_{62}/C_{36}D_{74}$ mixture by using small angle neutron scattering. This study has become one of subjects in this thesis and some as yet unresolved questions will be answered.

It is worth noting that there are investigations of paraffin multicomponent systems[58-59].

1.3 DYNAMICS OF PHASE SEPARATION

Figure (1.1) schematically shows typical phase diagrams. A phase separation of mixture systems on quenching starts from a homogeneous state and proceeds through a series of heterogeneous states, as is the case with the liquid-gas phase transition in one-component systems or with liquid-liquid or solid-solid phase separation in two-component systems. The processes can be divided into two main stages, early (including nucleation and growth regime) and later (including intermediate stage), depending on the degree of time evolution.

![Phase Diagrams](image)

Figure (1.1) Hypothetical phase diagrams: (left) a lower critical solution temperature (right) a upper critical solution temperature.

At the early stages, there are dominant concentration fluctuations in a homogeneous phase, and these lead to the birth of new phases. At the late stages, called the coarsening process, the size and number of new phases change neither nucleation of new phases nor variation in compositions, and the gradual aggregation of new phases occurs by what is called the coalescence. Finally, the entire system settles down to a macroscopic two phase
When a system is quenched to the metastable region, the region between the spinodal and binodal lines, as indicated in figure (1.1), small concentration fluctuations are damped because their growth causes an increase in free energy. Thus, in this, there is an energy barrier for the nucleation of a new phase. The system is unstable only for the rare, very large concentration fluctuations. Such concentration fluctuations are usually called nuclei or droplets. The nuclei are not in the equilibrium but tend to settle down to the equilibrium composition. Although there is an energy barrier, the new phase rapidly grows once it is formed. The mechanism leading to an equilibrium phase separation is called nucleus growth. When a system is brought into an unstable region, the spinodal decomposition takes place spontaneously without an energy barrier since any concentration fluctuations over a certain range of wavelengths reduce the free energy of the unstable system. The early stage of the spinodal decomposition can be described by Cahn-Hilliard-Cook equation [60-63]. This model avoids describing molecular details of systems and concentrates on describing kinetics of the phase separation using macroscopic variables. Despite some theoretical shortcomings of the original Cahn-Hilliard model, it has been widely used by experimentalists because of its simplicity and the fact that it quantitatively predicts some of the observed behavior.

It should be pointed out that the above discussion is based on the mean-field picture. In a real system the distinction between metastable and unstable regimes is not well defined, nevertheless the concepts retain some validity as a limiting behaviour. Theoretically, the general discussion is often based on the Ising model [64], for which the order parameter is simple enough for systems to be classified.

After some initial time following a quench, both the size and amplitude of the concentration grow. In the following late stage, the change in structure with time only depends on the growth of size and remains a self-similarity. The scaling relations of wavevector $Q_m$ at maximum scattering and of the scattering intensity $I_m(Q_mt)$ at $Q_m$ have been characterized as exponential forms for the time evolution of structure patterns

$$Q_m \propto t^{-\alpha}$$

(1.1)
and

\[ I_m \propto t^\alpha \]  \hspace{1cm} (1.2)

The values of the exponent \( \alpha \) listed in table 1.1 are predicted by various authors[65-70], depending on the different effects included by the particular theoretical approach.

In addition, the time evolution of a scattering function is investigated in terms of a scattering scaling law for the self-similarity between phase structures. According to Furukawa[71], the scattered intensity at a given time could be related to the scaled structure function \( S(\mathbf{x}) \) as follows

\[ I(Q, t) \propto V \langle \eta^2 \rangle \xi(t)^3 S(\mathbf{x}) \]  \hspace{1cm} (1.3)

<table>
<thead>
<tr>
<th>theoretical approaches</th>
<th>( \alpha )</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linearized theories</td>
<td>no growth</td>
<td>Cahn [65]</td>
</tr>
<tr>
<td>Nonlinear theories</td>
<td>0.21</td>
<td>Langer et al [66]</td>
</tr>
<tr>
<td>dynamic effects</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monte Carlo Ising model</td>
<td>0.21-0.25</td>
<td>Lebowitz et al [67]</td>
</tr>
<tr>
<td>Coalescence via constant volume evaporation</td>
<td>1/3</td>
<td>Binder et al [68]</td>
</tr>
<tr>
<td>Coalescence processes dominated by hydrodynamics effects</td>
<td>0.333</td>
<td>Lifschitz and Slyozov [69]</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>Siggia [70]</td>
</tr>
</tbody>
</table>

where \( V \) is the irradiated volume, \( \langle \eta^2 \rangle \) is mean square fluctuations of refractive indices (or scattering length density), and \( \mathbf{X} = Q\xi(t) \). Here \( \xi(t) \) is the correlation length which is related to the wavelength of periodic structure \( \Lambda(t) \) by the following equation

\[ \xi(t) = \Lambda(t) / 2\pi = 1 / Q_m(t) \]  \hspace{1cm} (1.4)

In the region where \( \langle \eta^2 \rangle \) is constant, the structure factor \( S(\mathbf{x}) \) can be described as

\[ S(\mathbf{x}) \propto I(Q, t) Q_m^3(t) \]  \hspace{1cm} (1.5)

Furukawa[72-73] also proposed another scaling theory in which the shape of structure function can be scaled by the following equation:
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\[ S(X) \propto \frac{(1 + \gamma/2)X^2}{\gamma/2 + X^{\gamma+2}} \]  \hfill (1.6)

Here \( \gamma \) is predicted to be equal to the dimension of a system \( d \) as

\[
\begin{align*}
\gamma &= d + 1 & \text{for an off-critical mixture} \\
\gamma &= 2d & \text{for a critical mixture}
\end{align*}
\]  \hfill (1.7)

If it is a three-dimensional growth, \( \gamma \) will be 6 and 4 for critical and off-critical mixtures, respectively. In the case of a two-dimensional growth, \( \gamma \) will be 4 and 3.

It is noted that a recent proposal\[74\] divides the kinetics of phase separation into four classes which are characterized by different low-temperature behaviour. Class 1 systems are similar to a simple Ising ferromagnet with spin-flip dynamics. In class 1 systems the domain size \( L(t) \) obeys familiar power-law domain growth: \( L(t)=t^\alpha \). The only difference in class 2 systems is that there is local defects which can cause freezing of the domain growth at absolute zero. Classes 3 and 4 have defects with domain size dependent activation energies. For classes 3 and 4, the domain size \( L(t) \) obeys a logarithmic growth: \( L(t)\propto(\log t)^m \). If \( m=1 \), systems belong to class 3 which may contain the random-field Ising model. Class 4 has \( m=1 \), and may include dilute ferromagnets and spin glasses.

The demixing in paraffin mixtures is very important because this system forms a bridge between conventional substances and macromolecules. In contrast to other chain systems in which phase separation has been studied, like polymer blends and alloys, the demixing process in paraffin mixtures takes place in a highly crystalline, anisotropic solid and involves some degree of conformational ordering\[49\].
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1.4 REFERENCES

2. A. Muller, Proc. R. Soc. A127, 417 (1930)
4. A. Muller, Acta Cryst. 1, 129 (1948)
6. A. Smith, J. Chem. Phys. 21, 2229 (1952)
Chapter 1 Introduction

38. R. Matheson and P. Smith, Polymer 26, 288 (1985)
40. D. Dorset, Macromolecules 18, 2158 (1985)
42. D. Dorset, Macromolecules 20, 2782 (1987)
64. K. Huang, Statistical Mechanics, Wiley, New York, 1963
70. E. Siggia, Phys. Rev. A20, 595 (1979)
2.1 THEORETICAL BACKGROUND OF SMALL ANGLE SCATTERING

Small angle scattering, including light scattering (SALS), x-ray scattering (SAXS), and neutron scattering (SANS), is an important technique in the study of the structure and dynamics of condensed matter. In this thesis, small angle x-ray scattering and small angle neutron scattering are used. For SAXS technique, the comprehensive reference is a monograph by Glatter and Kratky [1], but an earlier pioneering work of Guinier and Fournet is still very useful [2]. A excellent general reference about small angle neutron scattering is the article written by Kostorz [3]. The theory of small angle neutron scattering has been outlined by Price and Skold [4]. On particular subjects, for example the theory of the scattering from small defects is given by Schmatz [5]; the theory and application to colloidal solutions are described by Chen and Lin [6]; the theory and application to biological macromolecules are reviewed by Stuhrmann [7]; the scattering from fractals is summarized by Martin and Hurd [8]; and the scattering of catalysts is discussed by Brumberger et al [9]. Of particular relevance to this thesis, the theory and application to polymer system are reviewed by Higgins [10], and Higgins and Stein [11]. In these the similarities and underlying basis of equations are discussed. In this section, taking the small angle neutron scattering for an example, the main theoretical aspects of the small angle scattering are briefly reviewed. The equations will be introduced along with the discussion of specific applications.

The atomic scattering cross section from an assembly of atoms is written as

\[
\frac{d\sigma}{d\Omega} = \frac{1}{N} \sum_{\mathbf{R}} |b_{\mathbf{R}} \exp(i \mathbf{Q} \cdot \mathbf{R})|^2
\]

(2.1)

where \(N\) is the number of scattering nuclei exposed to the beam and \(b_{\mathbf{R}}\) the scattering length of the atomic species occupying a site with the position vector \(\mathbf{R}\). The wavevector \(\mathbf{Q}\) is defined as the difference between wavectors of incident and scattered neutrons. The
wavevector $Q = (4\pi/\lambda)\sin(\theta)$, where $\theta$ is the half scattering angle in experiments.

However, the essence of small angle neutron scattering is that the details of the scattering from individual atoms are lost, and scattering amplitude is replaced by its value averaged over many atomic spacings. Most SANS experiments are therefore interpreted using the scattering length density rather than the atomic cross section. Thus, the $b_r$ for atoms is replaced by a locally averaged scattering length density $\rho_b(\mathbf{r})$ where $\mathbf{r}$ is a continuously variable position vector, and the scattering process from individual particle can be written as

$$
\frac{d\sigma}{d\Omega} = \frac{1}{N} \left| \int V \rho_b(\mathbf{r}) \exp(iQ \cdot \mathbf{R}) d\mathbf{r} \right|^2
$$

(2.2)

It is furthermore convenient to express $\rho_b(\mathbf{r})$ in terms of its average value and fluctuations around the average:

$$
\rho_b(\mathbf{r}) = \bar{\rho}_b + \delta\rho(\mathbf{r})
$$

(2.3)

where $\bar{\rho}_b$ is averaged over volumes. Substituting equation (2.3) into equation (2.2), the cross section is thus given

$$
\frac{d\sigma}{d\Omega} = \frac{1}{N} \left| \int V \delta\rho(\mathbf{r}) \exp(iQ \cdot \mathbf{R}) d\mathbf{r} \right|^2
$$

$$
= \frac{1}{N} \left| \int V [\rho_b(\mathbf{r}) - \bar{\rho}_b] \exp(iQ \cdot \mathbf{R}) d\mathbf{r} \right|^2
$$

(2.4)

If a sample containing $N_p$ particles with a homogeneous scattering length density $\rho_p$ is embedded in a matrix of homogeneous scattering length density $\rho_m$, from equation (2.4), one obtains

$$
\frac{d\sigma}{d\Omega} = \frac{1}{N} (\rho_p - \rho_m)^2 \left| \int V_p \exp(iQ \cdot \mathbf{R}) d\mathbf{r} \right|^2
$$

(2.5)

where the integral is over all particles in a system. Equation (2.5) generally contains spatial and orientational correlations between particles, and effects due to size distributions. If all the particles are identical, the equation (2.5) can be written as

$$
\frac{d\sigma}{d\Omega} = \frac{V_p^2 N_p}{N} (\rho_p - \rho_m)^2 \left| F_p(Q) \right|^2
$$

(2.6)

with the single particle form factor
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\[ F_p(Q) = \frac{1}{V_p} \int_{V_p} \exp(iQ \Sigma r) \, dr \]  

(2.7)

where \( V_p \) is the particle volume. If the Q is extrapolated to zero, one can obtain

\[ \frac{d\sigma}{d\Omega}(Q \to 0) = \frac{V_p^2 N_p^2}{N} (\rho_p - \rho_m)^2 \]  

(2.8)

Many different particle form factors have been calculated. References 1. to 3. cover particular problems.

In the above formulae, the concentration of particles is assumed to be very dilute and interparticle interference is therefore neglected. However, in many cases, for example, polymer mixtures, colloidal systems, and aggregation systems, both single particle and interparticle effects can contribute to the cross section over whole range of interest. For a monodisperse system, the cross section can be written as

\[ \frac{d\Sigma}{d\Omega} = \frac{N_p}{V} |F(Q)|^2 \left( \sum_{i=1}^{N_p} \sum_{j=1}^{N_p} \exp(iQ(R_i - R_j)) \right) \]  

(2.9)

The quantities in equation (2.9) can be defined for clarity

\[ n_p = \frac{N_p}{V} \]

\[ P(Q) = |F(Q)|^2 \]

\[ S(Q) = \frac{1}{N_p} \left( \sum_{i=1}^{N_p} \sum_{j=1}^{N_p} \exp(iQ(R_i - R_j)) \right) \]  

(2.10)

and can be rewritten in a compact form as

\[ \frac{d\Sigma}{d\Omega} = n_p P(Q) S(Q) \]  

(2.11)

where \( S(Q) \) is the interparticle structure factor. As can be seen from equation (2.11), the cross section per unit volume is proportional to the particle density \( n_p \), and depends on the product of the intraparticle structure factor \( P(Q) \) and the interparticle structure factor \( S(Q) \) separately. This equation is the basis for the determination of the relative arrangement of large structure.
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For a polydisperse system of n components, the cross section may take a more complicated form. For spherical particles, the cross section can be expressed as

$$\frac{d\Sigma}{d\Omega} = \sum_{p=1}^{n} \sum_{q=1}^{n} \frac{N_p}{V} \frac{N_q}{V} F_p(Q)F_q^*(Q)S_{pq}(Q)$$  \hspace{1cm} (2.12)

where $N_p$ and $N_q$ are the numbers of particles of $p$th and $q$th components, respectively, and $S_{pq}(Q)$ is the particle structure factor defined by

$$S_{pq}(Q) = \frac{1}{\sqrt{N_p} \sqrt{N_q}} \left( \sum_{p=1}^{N_p} \sum_{q=1}^{N_q} \exp[iQ(R_{ip} - R_{jq})] \right)$$  \hspace{1cm} (2.13)

In principle the $S_{pq}(Q)$ may be obtained by solving the multicomponent Ornstein-Zernike equation[13]. At present, this has been done only for hard sphere systems[14] and for a symmetric electrolyte in the mean spherical approximation[15]. The equation(2.12) can also be written as a compact form

$$\frac{d\Sigma}{d\Omega} = \frac{N}{V} \left( \frac{1}{F(Q)} \right)^2 \bar{S}(Q) = n_p\langle P(Q) \rangle \bar{S}(Q)$$  \hspace{1cm} (2.14)

where

$$\langle P(Q) \rangle = \langle |F(Q)|^2 \rangle = \sum_{p=1}^{n} \frac{N_p}{N} \langle |F_p(Q)|^2 \rangle$$  \hspace{1cm} (2.15)

and

$$N = \sum_{p=1}^{n} N_p$$  \hspace{1cm} (2.16)

and

$$\bar{S}(Q) = 1 + \sum_{p=1}^{n_p} \sum_{q=1}^{n_q} F_p(Q)F_q^*(Q)(\frac{N_p}{V})(\frac{N_q}{V})\int_{0}^{\infty} (\frac{\sin Qr}{Qr})h_{pq}(r)4\pi r^2 dr$$  \hspace{1cm} (2.17)

where $h_{pq}$ is the total correlation function.

Another approach to deal with the polydispersity is to assume that the particle size and orientation are completely uncorrelated with particle positions[16], we can then write

$$\frac{d\Sigma}{d\Omega} = \frac{1}{V} \left( \sum_{i=1}^{N} \sum_{j=1}^{N} <F_i(Q)F_j^*(Q)> \exp[iQ\sum(R_i - R_j)] \right)$$  \hspace{1cm} (2.18)
Chapter 2  Experimental Techniques and Data Treatment

The compact form of equation (2.18) is given

\[
\frac{d\Sigma}{d\Omega} = \frac{N}{V} \langle P(Q) \rangle S(Q)
\]

where

\[
S(Q) = 1 + \frac{\langle F(Q)^2 \rangle}{\langle |F(Q)|^2 \rangle} \left[ \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \exp[iQ \cdot (\mathbf{R}_i - \mathbf{R}_j)] \right] - 1
\]

2.2 SMALL ANGLE NEUTRON SCATTERING, SANS

Small angle neutron scattering measurements throughout this thesis were made on the Small Angle Diffractometer (SAD) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory, USA, shown in figure (2.1). The detailed information about this instrument has been given elsewhere [17-18]. Pulsed neutron sources provide high effective neutron fluxes comparable to those available at high-flux research reactors. The small angle scattering of neutrons is detected, in fact, using the time-of-flight (TOF) method. A schematic diagram of the time-of-flight small angle instrument is illustrated in figure (2.2). The flight paths are determined to optimize flux and resolution and the dimensions are marked. A set of multiple focusing tapered collimator tubes is employed to increase the count rate at the detector. The collimation system consists of a bundle of seven individual tubes. Each tube is composed of two sections. The taper converges at the detector 300 cm beyond the sample position. A BF$_3$ monitor counter is inserted at the midpoint of the collimation sections. The detector is a two-dimensional position-sensitive gas proportional counter, filled with $^3$He and with an active area of approximately 17•17 cm$^2$, centered on the incident neutron beam. A 2.5 cm diameter aluminum cylinder, 5 cm long, and filled with $^6$Li$_2$CO$_3$, is positioned in front of the detector to act as a beam stop. The detector is partitioned into 64•64 cells across the active area. The intrinsic spatial resolution is about 2.5 mm. Temporal resolution could be adjusted by factors of two to provide from 1 to 256 channels. The number chosen during any experiment depends on the wavelength interval of interest and the anticipated time resolution requirements. Machine design-dependent parameters were refined in a Monte-Carlo code that produces estimates of the instrumental resolution function and available flux at the sample. The range of wavevector Q covered is 0.006<Q<0.3 Å$^{-1}$ and wavelengths, $\lambda$, between 2 and 14
Figure (2.1) The intense pulsed neutron source (IPNS) at the Argonne National Laboratory, USA.

Figure (2.2) Schematic diagram of time-of-flight small angle instrument at Argonne National Laboratory, USA [ref.18].

â€” are usually used in measurements. Since our samples are very strong scatterers, good scattering patterns could be typically recorded in half an hour or less. The sample thickness, 1 mm, is known precisely, therefore, all measurements are corrected to an absolute scale of scattered intensity using standard samples for the instrument calibration.
Figure(2.3) Schematic diagram of SAXS instrument at RSC, ANU.
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1.10

In Figure (2.4) Log-Log plot of $I$ versus $Q$ for 6% LUDOX sample.

Figure (2.5) SAXS Pattern of Milli-Q water at RSC, ANU.

2.3 SMALL ANGLE X-RAY SCATTERING, SAXS

Figure (2.3) depicts an original schematic arrangement of the small angle x-ray scattering apparatus at the Research School of Chemistry, ANU, aside from its computer system. This machine has been described elsewhere [19-20]. A small portion of the x-rays generated at the rotating anode pass through a beryllium window and a hole in a lead disc into a helium-filled brass guide tube before reaching the optics table. In order, the optics table holds the attenuator box, the mirror, the crystal monochromator, three pairs of slits and the sample. Some of the beam is scattered by the sample, which then passes through a large evacuated aluminum guide tube which has a beryllium window at its entry and a Mylar window at its exit. The direct unscattered beam is stopped by a small piece of tantalum at the exit of the aluminum guide tube, while the scattered x-ray passes into the
Chapter 2  Experimental Techniques and Data Treatment

one-dimensional position-sensitive detector (1-DPSD). At the present stage, the mirror has been moved and the beam directly passes through the slit 1 and 2.

SAXS data are presented as a function of the wavevector $Q$. For the RSC Huxley-Holmes camera, copper $K_\alpha$ radiation with $\lambda=1.54\,\AA$ is used. In principle, the wavevector $Q$ may cover the range from $0.009\,\text{Å}^{-1}$ to $0.6\,\text{Å}^{-1}$. The electronic background and detector sensitivity are corrected. Although the collimation system is a slit one due to removal of the mirror, the measured scattered intensity from smooth spheres is found to be proportional to $Q^{-4}$ rather than $Q^{-3}$. Figure (2.4) shows the scattering from colloidal silica, LUDOX as an example. This result may be due to very small height of the slits. The SAXS data, if necessary, may be further corrected for smearing effects due to the height of the beam and width of the slits, i.e., desmearing. However, the collimation system in this particular case is treated as a ‘hole collimation’. The absolute unit of scattered intensity can be obtained by comparison of the measured scattered intensity with that of Milli-Q water under the same optical alignment. Figure (2.5) shows the SAXS pattern of Milli-Q water.

2.4 PRELIMINARY DATA REDUCTION

Of interest to the studies in this thesis is the coherent scattering arising from scattering length density differences in the case of SANS and electron density differences in the case of SAXS. So, prior to data analysis, both SANS and SAXS data must be corrected for incoherent scattering and thermal density fluctuation scattering, respectively. An excellent reference about how to eliminate the incoherent scattering and thermal density fluctuation scattering is the article written by Koberstein, Morra, and Stein [21]. Both incoherent scattering and thermal density fluctuation scattering contributions to the observed scattering give rise to a constant background scattering, and at higher scattering angles, they dominate the scattering.

For pinhole collimation, the observed intensity $I_{\text{obs}}$ for a system showing such deviations from Porod’s law can be written
where $I_p(Q)$ is the intensity fall off as the reciprocal fourth power of the magnitude of the wavevector $Q$, i.e. familiar Porod law ($I(Q) \propto Q^4$) and $I_B(Q)$ background intensity resulting from thermal density of SAXS or incoherent scattering of SANS. The theoretical treatments for $I_B(Q)$ have been discussed\cite{22-24} and results are listed in the table 2.1. The factor $H^2(Q)$ is related to the Fourier transform of integral of density profile across the interfacial region. Ruland and Vonk's methods require scattering data in the high $Q$ region where the term $H^2(Q)$ has gone to zero. The factor $H^2(Q)$ is related to the Fourier transform of the integral of the density profile across the interface. In this thesis, the Bonart empirical relation is used for the elimination of background intensity.

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|}
\hline
Empirical Relation & Required Graph & Estimation of Parameter \\
\hline
Ruland: $I_B(Q) = C \exp(aQ^2)$ & $\ln I_B(Q)$ vs. $Q^2$ & $a$=slope, $C$=exp(inter.) \\
Vonk: $I_B(Q) = C + bQ^n$ & $I_B(Q)$ vs. $Q^n$ & $b$=slope, $C$=intercept \\
$n=2, 4, 6, \ldots$ & & \\
Bonart: $I_B(Q) = C$ & $Q^4I_{\text{obs}}(Q)$ vs. $Q^4$ & $C$=slope \\
\hline
\end{tabular}
\caption{Application of relations for determination of incoherent scattering (pinhole collimation)}
\end{table}
2.5 REFERENCES

Chapter 2  Experimental Techniques and Data Treatment


22. C. Vonk, J. Appl. Cryst. 6, 81 (1973)


1. INTRODUCTION

The study of paraffin solid solutions is not only important for understanding the properties of aliphatic chains in the condensed phase and with respect to solid solutions of organic molecules but also desirable for an understanding of the complicated problem of the denaturing and denaturing kinetics in biological systems. On the other hand, since these kinds of solutions form a bridge between conventional solutions and macromolecules, results generated may be heuristics for other systems. Of special interest is however, the C\text{12}H\text{25}, C\text{16}H\text{33}, mixture with melt crystallization at a ratio of 1:1 and its small angle X-ray scattering (SAXS). The results are of interest in connection with the importance and composition on the integrated scattering function and the percrystalline distortion and interfacial thickness between lamellae. On the basis of these results, the distribution of conformational disorder in the mixture is discussed.

3. EXPERIMENTAL DETAILS

The n-tridecane (C\text{12}H\text{25}) and n-hexadecane (C\text{16}H\text{33}) were obtained from Chemical Company while the n-heptadecane (C\text{17}H\text{35}) was obtained from Alfa. The samples have the molecular weights of 204, 268, and 308, respectively, and a determination of further purification was performed. The melting points of these compounds are

25
CHAPTER THREE STUDIES OF PARAFFIN MIXTURES BY SMALL ANGLE X-RAY SCATTERING

3.1 INTRODUCTION

The study of paraffin solid solutions is not only important for an understanding of properties of aliphatic chains in the condensed phase and with respect to the theory of solid solutions of organic molecules but also desirable for an unraveling of the complicated problem of the demixing and demixing kinetics in fractionated solids. On the other hand, since these kinds of solutions form a bridge between conventional substances and macromolecules, results generated may be heuristic for other systems. In this chapter, the C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}H\textsubscript{74} mixture with melt crystallization are studied by means of the small angle x-ray scattering (SAXS). The results are of interest in connection with effects of the temperature and composition on the integrated scattered intensity, the microstrain, the paracrystalline distortion, and over-all interfacial thickness between lamellae. On the basis of these results, the distribution of conformational disorder in the C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}H\textsubscript{74} mixture is discussed.

3.2 EXPERIMENTAL DETAILS

The n-triacontane (C\textsubscript{30}H\textsubscript{62}) and n-hexatriacontane (C\textsubscript{36}H\textsubscript{74}) were purchased from Aldrich Chemical Company while the n-tetracosane (C\textsubscript{24}H\textsubscript{50}) and n-tetracontane (C\textsubscript{40}H\textsubscript{82}) were obtained from FLUKA. The samples have the following purity grades: n-tetracontane>98%, n-hexatriacontane>98%, n-triacontane>99% and n-tetracosane>99%. No further purification was performed. The melting points of these samples are given in table 3.1. Paraffin mixtures were prepared by extensively mixing components of C\textsubscript{30}H\textsubscript{62} and C\textsubscript{36}H\textsubscript{74}. Subsequently the mixtures were heated for 2 hours in a oven at a temperature that is about 10°C higher than the melting point of the higher melting constituent. The mixtures thus prepared were injected into a temperature-controlled cell and very slowly cooled down to chosen temperatures. This cell is made of brass and consists of four layers of 0.025mm thick Mylar film. The sample was contained between the interior two-Mylar films with a thickness of 1mm and water was circulating through outer casings for
heating. The temperature was maintained at ±0.3°C during data collection. It took about one hour for the sample to reach thermal equilibrium. SAXS measurements were performed after the equilibrium was attained. For each concentration of the C₃₀H₆₂/C₃₆H₇₄ mixture, ageing times after slow cooling from the melt were not longer than 15 hours in order to avoid fractionation of the mixture[1]. In Chapter 4, SANS data will further confirm that under these experimental circumstances the phase separation does not take place.

<table>
<thead>
<tr>
<th>Sample</th>
<th>tetracontane</th>
<th>hexatriacontane</th>
<th>triacontane</th>
<th>tetracosane</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₀m(C)(label)</td>
<td>80 - 82</td>
<td>74 - 76</td>
<td>65 - 67</td>
<td>49 - 51</td>
</tr>
<tr>
<td>T₀m(C)*</td>
<td>82.1</td>
<td>76.2</td>
<td>66.5</td>
<td>50.3</td>
</tr>
</tbody>
</table>

* The average melting points were measured using hot stage microscope

3.3 SCATTERING PATTERNS

3.3.1 C₃₀H₆₂ PATTERNS

SAXS measurements of the n-triacontane(C₃₀H₆₂) were carried out at four temperatures. The maximum temperature used was 61.5°C, about 4.5 degrees below the melting point.

Figure(3.1) SAXS patterns of C₃₀H₆₂ at different temperatures
Three orders of the small angle long spacing diffraction were obtained, as shown in figure (3.1). The curves have been shifted up for clarity.

### 3.3.2 $C_{36}H_{74}$ PATTERNS

SAXS patterns from the hexatriacotane were obtained at five temperatures. Figure (3.2) exhibits observed scattered intensity as a function of wavevector at different temperatures. The SAXS results display rather complex scattering patterns which are the same as those observed by Sullivan and Week[3]. Several subsidiary peaks appear near main orders. The scattering pattern is more complex at low-temperature than that at high-temperature. As the temperature increases, some of subsidiary peaks disappear or decrease.

![Figure(3.2) SAXS patterns of $C_{36}H_{74}$ at different temperatures](image)

### 3.3.3 $C_{30}H_{62}/C_{36}H_{74}$ PATTERNS

Figure (3.3) shows representative scattering patterns of the $C_{30}H_{62}/C_{36}H_{74}$ mixture at several compositions and different temperatures. The curves have also been shifted up for clarity. Three orders are observed. Generally, the observed scattered intensity of the mixture is larger than that of the two pure components. The positions of the peaks are found to depend on both composition and temperature. It can be seen that the width at half height of peak becomes narrower at higher temperatures. No subsidiary peaks are observed around the main peaks.
Chapter 3  Studies of Paraffin Mixtures by SAXS

![Graphs showing SAXS data for 10%, 20%, 40%, and 50% paraffin mixtures at various temperatures.](image-url)
Figure (3.3) SAXS patterns of the \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{H}_{74} \) mixture at different temperatures. Compositions of \( \text{C}_{36}\text{H}_{74} \) from top to bottom are 0.1, 0.2, 0.4, 0.5, and 0.8.

### 3.4 DATA ANALYSIS

The scattered intensities in this study refer to integrated intensities. Methods used for data analysis are: (1) the Fourier analysis of multiple orders [4,5], the Warren-Averbach procedure, (2) the paracrystalline analysis [6,7], the treatment of Hosemann, and (3) electron density analysis [8], the model of Strobl et al.

#### 3.4.1 INTEGRATED SCATTERED INTENSITY

The integrated intensity is calculated by the Igor computer program. Lower and upper limits of a integration are chosen from \( 2\pi(m+1/2)/L \) to \( 2\pi(m-1/2)/L \) unless noted, where \( m \) is a order number and \( L \) the long spacing. Figure (3.4) shows an typical integrated curve.
calculated by the computer program. The lower and upper limits of the integration have been indicated in the figure.

### 3.4.2 FOURIER TRANSFORM ANALYSIS

Warren and Averbach [4] and Warren [5] treated the X-ray diffraction profile which is assumed to be given by the convolution product of a profile due entirely to crystallite size and of a profile due only to lattice distortion. They showed that the mth-order hkl peak could be expressed as a Fourier series over harmonic numbers n in which the coefficients of the cosine $A_n$ and sine $B_n$ terms are given. Because displacements are symmetric about zero, one usually observes that the sine coefficients $B_n$ are very small. Therefore, the broadening of the peak is represented only by the cosine coefficients. The Stokes-corrected Fourier cosine coefficients $A_n$ of profiles are given as follows:

$$A_n(\xi, Q) = A_0(\xi) \cdot A_D(\xi, Q)$$  \hspace{1cm} (3.1)

where $A_n(\xi, Q)$, $A_0(\xi)$, and $A_D(\xi, Q)$ are the Fourier transforms of corrected experimental profile, the crystallite size profile, and the distortion profile, respectively. $Q$ is the wavevector as usual. If the variables $n$ and $Q$ are small, the $A_0(\xi, Q)$ can be exponentially approximated. Thus, equation (3.1) can be written in the following form (normalized to $A_0=1$) in terms of the order $m$ of the reflection.

$$\ln A_n(\xi, Q) = \ln A_0(\xi) - 2\pi^2 < E^2 > \xi^2 m^2 / L_{(m=1)}^2$$  \hspace{1cm} (3.2)

where the term $\xi=na$, $a$ is the period of the Fourier analysis, $L_{(m=1)}$ is the long spacing for the first order peak. The term $<E^2>$ is the microstrain, a random, local lattice distortion, averaged over all distances $\xi$, normal to the diffracting planes and under the x-ray beam. The maximum value of the microstrain $<E>_{\text{max}}$ is given by [9]

$$< E >_{\text{max}} \equiv 1.25 < E^2 >^{1/2}$$  \hspace{1cm} (3.3)

As shown by Bertaut [10], in deriving equation (3.1), each crystal is envisioned to be composed of columns parallel to $\xi$. Each column is composed of a stack of unit cell sufficient in number to traverse the crystal from one surface to the other. For all columns with $i$ cells, $A_0(\xi)$ could be expressed.
\[
A_s(\xi) = \frac{1}{N} \int_{i=0}^{\infty} (i-1|\xi|) p(i) \, di
\]  

(3.4)

where \( p(i) \) is the number of columns per unit length and \( N \) is the total number of unit cells. The derivative of \( A_s(\xi) \) with respect to \( \xi \) at \( \xi=0 \) is

\[
\left( \frac{dA_s(\xi)}{dt} \right)_{\xi=0} = -\frac{1}{N} \int_{i=1}^{\infty} p(i) \, di = \frac{N_s}{N} = \frac{1}{N}
\]  

(3.5)

where \( N_s \) is the total number of columns in the crystallite.

Thus, in terms of equation (3.2), a plot of \( \ln A_n \) versus \( m^2 \) for each \( \xi \) will produce a straight line for small \( \xi \). The slope gives the \( 2(\pi a)^2 \langle \varepsilon^2 \rangle / L^2 \) from which the mean-square microstrain \( \langle \varepsilon^2 \rangle \) can be obtained. The intercept on the ordinate yields \( \ln A_s \). Then, in terms of equation (3.5), the intercept on the abscissa of the initial slope of \( A_s \) versus \( \xi \) produces the mosaic domain size when \( A_s \) is normalized to a maximum value of unity. It is noted that at least three orders of reflection are necessary to make accurate results.

For a practical evaluation of the Fourier coefficients, a Fourier interval \( AOB \), shown schematically in figure (3.5), is selected. We believe that this interval is large enough to include measurable tails of a peak. In order to eliminate uncertainties associated with the

![Figure 3.5](image-url)

Figure (3.5) Relation between the experimental diffraction peak and the interval AOB within which it is expressed as a Fourier series.
coefficients having the lowest harmonic numbers, a appreciated plotting range can be selected with a plot of \( \ln A_n \) versus \( n \), as proposed by Rothman and Cohen[11], before the Warren-Averbach method is used. Figure(3.6) shows representative plots of \( \ln A_n \) versus \( n \) for three peaks of \( 2/8 \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{H}_{74} \) mixture at room temperature. The Warren-Averbach method is then applied within the linear portion determined by the plot of \( \ln A_n \) versus \( n \).

### 3.4.3 PARACRYSTALLINE ANALYSIS

Hosemann[6] has discussed a method of separating size from distortion broadening in which paracrystalline lattice distortions are responsible for a portion of the observed line broadening. The method has been extended to polymer systems by Bonart, Hosemann, and McCullough[7]. The integral breadth is given

\[
\delta \beta^2 = \left( \frac{1}{D} \right)^2 + \left( \frac{1}{2L} \left[ 1 - \exp(-2\pi^2 g^2 m^2) \right] \right)^2
\]

or

\[
\delta \beta = \frac{1}{D} + \frac{(\pi gm)^2}{L}
\]

where \( g \) is the paracrystalline distortion defined as the mean statistical fluctuation between net-planes, \( D \) paracrystalline size. In deriving above expressions, both size and distortion profiles are assumed to be Gaussian. It should be pointed out that the distortion
parameter obtained from the paracrystalline analysis may be quite different from that obtained from the Fourier transform method although both methods are precisely defined[9]. The situation may be further complicated by the simultaneous presence of both size and distortion[9]. In practice, the integral breadth can be replaced by the width at half height of a peak[12].

3.4.4 ELECTRON DENSITY ANALYSIS

Figure(3.7) schematically shows perfect and defect paraffin lamellar structures. The corresponding electron density profiles are shown in figure(3.8). Strobl et al [8] have analyzed the defect structures and molecular motion in paraffins in terms of electron density variations. Craievich et al[13] have investigated the molecular motion and conformational defects in odd-numbered paraffins with 19≤carbon numbers≤27 as a function of the temperature.

For small angle x-ray scattering analysis, the electron density in a paraffin or a paraffin mixture can be essentially a constant \( \eta_c \) in all the volume except interface regions which constitute layer vacancies. The scattered intensities of the reflections can be described by the electron density difference

\[
\Delta \eta(z) = \eta_c - \eta(z)
\]

where \( \eta(z) \) is the average electron density in a plane parallel to the interface at a distance \( z \) from the center of gravity of the \( \Delta \eta(z) \) function. In the case of a perfect crystal the average electron density has a rectangular shape

\[
\Delta \eta(z) = \eta_c - (\varepsilon / d_s) \quad \text{if} \quad |z| < d_s / 2
\]

\[
= 0 \quad \text{if} \quad |z| > d_s / 2
\]

with

\[
d_s = L - L_k \cos \phi
\]

where \( L \) is defined as a long spacing between successive interfaces. For pure paraffins, \( L_k \) is fully extended chain length along which the electronic density is a constant \( \eta_c \). For paraffin mixtures, \( L_k = \phi_1 L_1 + (1 - \phi_1) L_2 \), \( \phi_1 \) is a molar volume fraction of specie 1. \( \phi \) is the tilting angle enclosed by the axis and the surface normal. Thus, \( d_s \) is the thickness of the vacancy layers, \( \varepsilon / d_s \) is a correction due to the contribution the electron density in the
Figure (3.7) Schematic diagrams of paraffin lamellar structures: (a) perfect crystal, (b) intrachain defects, and (c) longitudinal disorder (intrachain defects is not shown for clarity). One circle represents several carbon numbers.

voids from the methyl terminal groups. \( \varepsilon \) denotes the corresponding electron density and follows from the cross section per chain \( S \).

\[
\varepsilon = \frac{2}{S} \cos \varphi
\]  

(3.11)

For a non ideal structure, the integral and the second moment of \( \Delta \eta(z) \) can define two parameters.
\[ \kappa = \int \Delta \eta(z) \, dz \]  
(3.12)

describes the total electron density per square, and

\[ \sigma^2 = \frac{1}{\kappa} \int z^2 \Delta \eta(z) \, dz \]  
(3.13)

According to Strobl et al[8], the scattered intensity in a absolute unit \( I(Q) \) of the reflections 001 are associated with the structure factor \( B_m \) by

\[ I(Q) = B_m^2 \]  
(3.14)

where \( B_m \) is defined by

\[ B_m^2 = [\int \Delta \eta(z) \exp(2\pi i m z/L) \, dz]^2 \]  
(3.15)

An appropriate extrapolation to the origin \( Q=0 \) of the scattering intensities of the several order reflections (\( m=1, 2, 3, \cdots \)) leads to

\[ B_m^2(Q=0) = \kappa^2 \]  
(3.16)

and \( \sigma^2 \) using the relation

\[ \frac{d^2 B_m^2}{dQ^2}_{|Q=0} = -8\pi^2 \kappa^2 \sigma^2 \]  
(3.17)

![Figure 3.8](image_url)

Figure (3.8) Schematic \( \Delta \eta \) functions for (a) perfect crystals, (b) crystals with only longitudinal molecular motion, and (c) crystals containing molecules with conformational defects.

The average local thickness \( d_{av} \) and over-all thickness \( D_t \) of the interfacial region can be obtained by

\[ d_{av} = \frac{(\kappa + \varepsilon)}{\eta_c} \]  
(3.18)
and

\[ D_t = \sqrt{12\sigma} \]  

(3.19)

If \((\sqrt{12\sigma m/L})^4 << 1\) for all the observed 00l reflections, the mean square of the structure factor \(B_m\) has a parabolic form

\[ B_m^2 = \kappa^2 - 4\pi^2\kappa^2\sigma^2(m/L)^2 \]  

(3.20)

and the parameters \(\sigma\) and \(\kappa\) can be determined. If this condition is not fulfilled a least-squares fitting of the experimental intensities, a higher-degree polynomial is needed to obtain the parameters

\[ B_m^2 = C_0 + C_2m^2 + \cdots + C_{2n}m^{2n} \]  

(3.21)

3.5 INTERPRETATION OF DATA AND DISCUSSION

3.5.1 LONG SPACING

By application of Bragg's law to the first peaks, the long spacings are obtained. Figure (3.9) shows the plot of long spacing as a function of composition at room temperature for the \(C_{30}H_{62}/C_{36}H_{74}\). Clearly, 'new' SAXS spacings are intermediate in length between the pure \(C_{30}H_{62}\) and \(C_{36}H_{74}\) components and lie somewhat above Vegard's law line. The variation of equilibrium long spacing with composition for the same mixture was investigated by Dorset [1, 14]. It has been found that for equilibrium samples in which the separated lamellae are found, the relationship between the long spacing and composition is strictly linear in accord with the exact Vegard's law.

Figure (3.9) The long spacing of the \(C_{30}H_{62}/C_{36}H_{74}\) mixture as a function of composition at room temperature. For pure \(C_{30}H_{62}\), the circle is the long spacing of the monoclinic phase; the square is the long spacing of the orthorhombic phase [14].

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The experimental temperature dependence of the long spacing of pure $C_{30}H_{62}$ is plotted in figures (3.10). In the range of experimental temperature, the long spacing of $C_{30}H_{62}$ is a constant. The long spacings of $C_{30}H_{62}$ were reported to be 35.8Å in the monoclinic phase and 40.0Å[15] or 41.2Å[14] in the orthorhombic phase. Comparing experimental long spacings with literature values, the sample is found to be in the monoclinic phase. Differential thermal analysis (DTA) and x-ray studies have indicated that the temperature of the crystalline to the rotator phase transition is 61.6°C for $C_{30}H_{62}$[2, 16]. The maximum temperature, at which we have recorded as data was 61.5°C, is close to this temperature.

**TABLE 3.2 The monoclinic long spacing of $C_{30}H_{62}$**

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>L(m=1)</th>
<th>L(m=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>35.84</td>
<td>35.58</td>
</tr>
<tr>
<td>37.5</td>
<td>35.84</td>
<td>35.58</td>
</tr>
<tr>
<td>44.1</td>
<td>35.84</td>
<td>35.58</td>
</tr>
<tr>
<td>61.5</td>
<td>35.84</td>
<td>35.58</td>
</tr>
</tbody>
</table>

![Figure 3.10](image) The monoclinic long spacing obtained from the first order as a function of temperature for $C_{30}H_{62}$

**TABLE 3.3 The orthorhombic long spacings of $C_{36}H_{74}$**

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>L(m=1)</th>
<th>L(m=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>48.53</td>
<td>47.72</td>
</tr>
<tr>
<td>54.5</td>
<td>48.53</td>
<td>47.72</td>
</tr>
<tr>
<td>63.4</td>
<td>48.53</td>
<td>47.72</td>
</tr>
<tr>
<td>69.5</td>
<td>47.15</td>
<td>46.38</td>
</tr>
<tr>
<td>74.0</td>
<td>46.46</td>
<td>46.06</td>
</tr>
</tbody>
</table>

The data taken on the first and second peaks of $C_{36}H_{74}$ are given in table 3.3. Figure (3.11) shows the long spacing of the orthorhombic phase as a function of temperature. The long spacing is found to decrease at high-temperature in the measured range. The long
spacings of subsidiary peaks near the first order are calculated to be 42.8Å and 39.6Å, respectively. The long spacings of monoclinic $M_{011}$ and $M_{201}$ phases were reported to be 42.3Å and 39.3Å\cite{3}. Comparing experimental long spacings with literature values, the sample is found to be a mixture of phases.

![Figure 3.11](image)

**Figure (3.11)** The orthorhombic long spacing of the first order as a function of temperature for $C_{36}H_{74}$

The variation of the long spacing with temperature is also shown in figures (3.12) and (3.13) for $C_{24}H_{50}$ and $C_{40}H_{82}$, respectively. The purpose of these measurements was to test if the variation of the long spacing of longer and shorter paraffins with temperature is different. As seen from these figures, the long spacing of $C_{24}H_{50}$ remains constant 30.2Å while the long spacing of $C_{40}H_{82}$ has the same behavior as that of $C_{36}H_{74}$ in the range of experimental temperature. Even if the temperature is raised further for $C_{24}H_{50}$, the long spacing should increase rather than decrease because of the transition of the sample from the crystalline to the rotator phase in which the long spacing was reported to be 32.85Å\cite{17}. The main outcome of all these results is that it seems proven that at high-temperature, the introduction of the conformational disorder to longer chain paraffins could be easier than that to shorter chain paraffins and this may cause c-axis shortening.

![Figure 3.12](image)

**Figure (3.12)** The long spacing of the first order as a function of temperature for $C_{24}H_{50}$
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Figure (3.13) The long spacing of the first order as a function of temperature for C_{40}H_{82}.

3.5.2 THE INTEGRATED SCATTERED INTENSITY

3.5.2.1 C_{30}H_{62}

The peaks in figure (3.1) are enlarged in order to clearly observe the change in the scattered intensity with increasing temperature. Figure (3.14) shows representative results. The integrated intensities obtained from the first (I_1) and second (I_2) peaks in terms of figure (3.4) are listed in table 3.4. Plots of the integrated intensity of the first peak as a function of temperature is shown in figure (3.15). It can be seen that in the range of experimental temperature, the integrated intensity does not vary with increasing temperature.

![Figure 3.14](image)

**Figure (3.14) The first orders of C_{30}H_{62} at different temperatures**

**Table 3.4 The integrated intensity of C_{30}H_{62}**

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>I_1</th>
<th>I_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>140.4</td>
<td>46.5</td>
</tr>
<tr>
<td>37.5</td>
<td>138.9</td>
<td>43.5</td>
</tr>
<tr>
<td>44.1</td>
<td>139.2</td>
<td>42.7</td>
</tr>
<tr>
<td>61.5</td>
<td>136.7</td>
<td>45.1</td>
</tr>
</tbody>
</table>
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Figure (3.15) The integrated intensity of the first order of $C_{30}H_{62}$ as a function of temperatures

temperature. This corresponds to a temperature independent of the long spacing. The result obtained from the second order is very similar to that found from the first.

3.5.2.2 $C_{36}H_{74}$

In figure (3.16), the first order peaks at temperatures of 25°C, 56.7°C, and 74°C are enlarged so as to clearly show the intensity dependence of temperature. The integrated ranges are chosen from $2\pi(m+1/2)/L$ to $2\pi(m-1/2)/L$ and from main peaks. The integrated intensities are given in table 3.5. The plot of the integrated intensity obtained from the first main peak ($I_1$) as a function of temperature is presented in figure (3.17). It can be seen from the $C_{36}H_{74}$ data that in contrast to $C_{30}H_{62}$, the increase in the integrated intensity with increasing temperature is accompanied by a decrease in the orthorhombic long spacing in the range of measured temperature.

Figure (3.16) The first orders of $C_{36}H_{74}$ at different temperatures
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### TABLE 3.5 The integrated intensity of C\(_{36}H_{74}\)

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>I(_1)</th>
<th>I(_2)</th>
<th>I(_1)'</th>
<th>I(_2)'</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>73.4</td>
<td>16.2</td>
<td>173.2</td>
<td>45.5</td>
</tr>
<tr>
<td>54.5</td>
<td>85.3</td>
<td>18.7</td>
<td>157.4</td>
<td>40.0</td>
</tr>
<tr>
<td>63.4</td>
<td>103.1</td>
<td>20.5</td>
<td>176.0</td>
<td>45.0</td>
</tr>
<tr>
<td>69.5</td>
<td>109.2</td>
<td>24.6</td>
<td>171.7</td>
<td>46.8</td>
</tr>
<tr>
<td>74.0</td>
<td>157.4</td>
<td>38.9</td>
<td>209.4</td>
<td>62.5</td>
</tr>
</tbody>
</table>

I\(_1\)' obtained from the Q range from 2\pi(m+1/2)/L to 2\pi(m-1/2)/L

![Figure 3.17](image-url) The integrated intensity of the first peak as a function of temperature for C\(_{36}H_{74}\).

3.5.2.3 C\(_{36}H_{74}/C\(_{30}H_{62}\)

In general, the temperature effect we have observed on the scattered intensity of mixtures is the same as that observed in the case of pure paraffins, that is to say, the integrated intensity increases with increasing temperature. The enlarged reflection orders of the C\(_{30}H_{62}/C\(_{36}H_{74}\) mixtures at several temperatures are shown in figure(3.18). Plots of the integrated intensity, corresponding to the first orders of curves in figure(3.18), are displayed as a function of the temperature in figure(3.19). The integrated intensity is found to increase with increasing temperature. The plot of the integrated intensity as a function of the composition at room temperature is shown in figure(3.20). The integrated intensity shows its maximum in the range of C\(_{36}H_{74}\) composition between 40% and 50%.

According to Sullivan et al[3] and Strobl et al[8], the increase in the scattered intensity with increasing temperature may be occurred by several mechanisms which cause the contrast of the electron density to be larger:
Figure (3.18) The first peaks of SAXS patterns of the C$_{30}$H$_{62}$/C$_{36}$H$_{74}$ mixture at different temperatures. Compositions of C$_{36}$H$_{74}$ are: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.5, (e) 0.6, and (f) 0.8.
Figure (3.19) The integrated intensity as a function of temperature for $C_{36}H_{64}/C_{36}H_{74}$ mixtures. Compositions of $C_{36}H_{74}$ are: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.5, and (e) 0.8.
(1) Thermal expansion of the lamellar distance is one mechanism. However, theoretical analysis shows the intensity increase resulting from thermal expansion is too small to yield the large increase in the scattered intensity observed in experiments[3]. Rotations of chains into subsidiary potential-energy minima could give rise to orientational disorder and yield defects in the sublattice which is methylene units arranged in subcells. This orientational disorder may influence the scattered intensity.

(2) Vacancies are introduced if regular zig-zag conformation of chains is interrupted, e.g., chains are contracted. When one molecular chain is contracted, the direction of unperturbed parts along this chain still remain linear in order to satisfy the packing requirements. Defects with this particular conformation are termed kink defects or Reneker defects. Vacancies are also introduced by the shifting of chains along their axes, longitudinal disorder, as shown in b and c of figure(3.7). The longitudinal disorder may be accompanied by the defects from contracted chains.

(3) The increase in scattered intensity with increasing temperature may be also caused by the molecular tilting due to solid-solid phase transitions. As it is known, different crystal phases have different end-group packing and lamellar distances. When a solid-solid phase transition takes place, the scattered intensity of 001 maxima will show up this
change. If the solid-solid phase transition is not complete, end-group mismatch occurs because molecular chains make contact with different phases. The scattered intensity is therefore enhanced due to the poorer end-group packing. On the other hand, solid-solid phase transitions often occur together with a continuous increase of orientational disorder and a consequent decrease of lateral molecular interaction, which may contribute to the increase of longitudinal molecular motion and make lamellar boundaries further complications.

3.5.3 FOURIER TRANSFORM ANALYSIS

Plots based on the Warren-Averbach Fourier transform method are shown in figure (3.21) for $\text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{H}_{74}$ mixture at room temperature. The plot of $\ln A_n$ versus $m^2$ is a straight line for small order numbers. As $m$ increases, the plot should show a curvature, as observed by Buchanan and Miller [18], Wecker et al [19]. The extrapolation procedure can be done in terms of equation (3.2) for several $\xi$ within which a plot of $\ln A_n$ versus $n$ yields a straight line. A similar feature is observed for the samples at other temperatures. A set of the microstrain parameters, $<E^2>^{1/2}$, is calculated from the slopes and parameters $A_s$ are obtained from the intercepts. Figure (3.22) shows $A_s$ data as a function of $\xi$ for these samples. The mosaic domain size is obtained from the intercept on the abscissa in the plot of $A_s$ versus $\xi$ in terms of equation (3.5).

Figure (3.23) shows the variation of the microstrain $<E^2>^{1/2}$ with $\xi$ for the $\text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{H}_{74}$ mixture at room temperature. For each composition, $<E^2>^{1/2}$ decreases rapidly with increasing $\xi$ and then tends to level off. The same behavior has been reported in the literature [18-19]. Two explanations of this behavior have been suggested by Warren [20]: one arises from inhomogeneous microstrain; and the other is that as the $\xi$ increases, the microstrain from the contribution of smaller domains is no longer significant. The microstrain in smaller domains is likely to be larger [20].

Figure (3.24) shows the variation of the microstrain $<E^2>^{1/2}$ at harmonic number $n=3.494$ with the composition of $\text{C}_{34}\text{H}_{74}$ in the $\text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{H}_{74}$ mixture at room temperature. The data are fitted by a least-squares method. As seen from the figure, the microstrain,
Figure (3.21) Plots of LnA_n versus m^2 for the C_{30}H_{62}/C_{36}H_{74} mixture at room temperature. Compositions of C_{36}H_{74} are: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4, (e) 0.6, and (f) 0.8.
Figure (3.22) Plots of $\ln A_s$ versus $na$ for the $C_{30}H_{62}/C_{36}H_{74}$ mixture at room temperature. Compositions of $C_{36}H_{74}$ are (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4, (e) 0.6, and (f) 0.8.
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Figure (3.23) The microstrain \( \langle E^2 \rangle^{1/2} \) is plotted as a function of \( \frac{1}{n} \) for the \( C_{36}H_{74}/C_{30}H_{62} \) mixtures at room temperature. The error limit is about \( \pm 1.5\% \).

Figure (3.24) The microstrain \( \langle E^2 \rangle^{1/2} \) \( (n=3.494) \) is plotted as a function of the composition of \( C_{36}H_{74} \) at room temperature. The error limit is about \( \pm 1.5\% \).

Figure (3.25) The domain size is plotted as a function of the composition of \( C_{36}H_{74} \) at room temperature. The error limit is about \( \pm 2.0\% \).
Figure (3.26) The microstrain $<E^2>^{1/2}$ is plotted as a function of temperature for $\text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{H}_{74}$ mixtures. Compositions of $\text{C}_{36}\text{H}_{74}$ are: (a) 0.2, (b) 0.3, (c) 0.4, (d) 0.6, and (e) 0.8. Harmonic numbers $n$ are $\Box 3.494$, $\star 6.988$, $\blacksquare 10.482$, and $\diamond 13.977$. The error limit is about ±1.5%.
$<E^2>^{1/2}$, increases by mixing and is at its maximum in the range of $C_{36}H_{74}$ composition from 40% to 50%, which falls in a similar composition range where the integrated intensity shows a maximum. The plot of domain size as a function of $C_{36}H_{74}$ composition is shown in figure(3.25). It is noted that a slight reduction in the domain size occurs in the range of $C_{36}H_{74}$ composition from 40% to 60%. These results imply the local lattice distortions over the distance $\xi$ reach their maximum around this composition range.

Plots of the microstrain $<E^2>^{1/2}$ as a function of temperature at several harmonic numbers $n$ are shown in figure(3.26). The calculated $<E^2>^{1/2}$ values are basically independent of temperature, if anything, a slight reduction at high-temperature. This behavior may be associated with the distribution of the disorder in lamellae. More discussions of this point will be given.

3.5.4 PARACRYSTALLINE ANALYSIS

The results obtained by the paracrystalline analysis are shown in figure(3.27) in terms of equation(3.7) for $C_{30}H_{62}/C_{36}H_{74}$ mixtures at room temperature. The integrated width is replaced by the half-height width. The linearity of these plots confirms the presence of paracrystalline distortions along the mixture macrolattice. This means that the lamellae are not uniformly separated and therefore the macrolattice distance has a statistical fluctuation. The similar results are also observed for the samples at other temperatures. The paracrystalline distortion $g$ of this macrolattice can be obtained from the slope of $\delta \beta$ versus $m^2$ plot. The plot of the paracrystalline distortion $g$ as a function of $C_{36}H_{74}$ composition at room temperature is shown in figure(3.28). As can be seen, the paracrystalline distortion $g$ also increases by mixing and is at its maximum in the range of around 40% $C_{36}H_{74}$, which is in agreement with the results obtained from both the integrated intensity and the microstrain. The relationship between the degree of the distortion and the composition is thus confirmed.

Figure(3.29) shows the representative paracrystalline analysis for 3/7 and 8/2 $C_{10}H_{62}$ /$C_{36}H_{74}$ mixtures at several temperatures. The slopes in the figure are found to decrease with increasing temperature. Plots of the paracrystalline distortion $g$ as a function of
Figure (3.27) The paracrystalline analysis of SAXS reflections for \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{H}_{74} \) mixtures at room temperature. Compositions of \( \text{C}_{36}\text{H}_{74} \) are: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.6, and (e) 0.8. The error limit is about \( \pm 5\% \).
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Figure (3.28) The plot of g factor as a function of composition at room temperature. The error limit is about ±10%.

Figure (3.29) The paracrystalline analysis for 3/7 (upper) and 8/2 (down) \(C_{36}H_{74}/C_{30}H_{62}\) mixtures at different temperatures. The error limit is about ±10%.
temperature are shown in figure (3.30) for different compositions. As the temperature increases, the $g$ value is a constant at first and then decreases, indicating the mean statistical fluctuation between lamellae decreases as the temperature increases. These data are in disagreement with the results obtained from linear and branched polyethylene [21]. The analysis of the paracrystalline method to these polyethylene [21] yields the conclusion that the paracrystalline distortion $g$ is independent of temperature.

### 3.5.5 ELECTRON DENSITY ANALYSIS

The electron density analysis is limited to obtaining the parameter $D_t$, the over-all thickness of the interfacial region, in terms of equation (3.21). The goal of this analysis is simply to learn how the parameter $D_t$ varies with increasing temperature. Figure (3.31)
Figure (3.31) Plots of the square of the structure factors obtained from SAXS of 2/8 C₃₀H₆₂/C₃₆H₇₄ mixture. Solid lines are fourth-order polynomials obtained by least-squares fitting in terms of equation (3.21). The error limit is about ±1.5%.

Figure (3.32) Plots of the normalized Dₜ as a function of temperature for C₃₀H₆₂/C₃₆H₇₄. Compositions of C₃₆H₇₄ are: (a) 0.2, (b) 0.3, (c) 0.4, and (d) 0.8. The error limit is about ±1.5%.
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Figure (3.33) Plots of the normalized $\kappa$ as a function of temperature for $C_{30}H_{62}/C_{36}H_{74}$ mixtures. Compositions of $C_{36}H_{74}$ are: (a) 0.2 and (b) 0.5. The error limit is about ±15%.

shows representative plots. The parameters are obtained from extrapolated values and the slopes of a fourth-order polynomial for the structure factor[8,13]. Experimental temperature dependence of the normalized parameter $D_1$ and $\kappa$ are plotted in figures (3.32) and (3.33), respectively, for several compositions. The feature related to these parameters is their increase as the temperature increases, which is in agreement with the results obtained from pure paraffins[8,13].

3.5.6 DISCUSSION

According to the information collected from the long spacing, the integrated scattered intensity, the microstrain, the paracrystalline distortion, and the interfacial region, we are in the position to discuss the distribution of conformational disorder in lamellae.

There are two quite different models proposed to describe the location of chain conformational disorder induced by mixing in paraffin mixtures. Lauritzen et al[22] have suggested that the disorder is located at chain ends and involves a gauche-bond formation which minimizes vacancy volume in chain end regions. Blasenbrey and Pechhold[23] have proposed a different model in which disorder mainly occurs in chain interiors. The imperfections in paraffin mixtures could be associated with the chain end disorder arising from the chain length mismatch between two pure components and with kinks in lamellae. The former disorder is highly dependent on the composition while the latter one is nearly independent of the composition[24,25].
Snyder et al.[24] found that for a shorter chain mixture, C19/C21, in both the low-temperature phase (orthorhombic phase) and the high-temperature phase (hexagonal phase), chain conformational disorder induced by mixing is confined to the region nearest chain ends and that the chain interior is relatively unaffected. The chain conformational disorder shows a maximum near 1:1 molar composition. For a longer chain mixture, C46/C50, in the low-temperature phase (near 27°C), Snyder et al.[25] also found that the nature of the disorder is very similar to that of C21/C19 mixture.

Bonsor and Bloor[26] have reported the variation of measured bulk density of C21H44/C23H48 mixture with composition. Retief et al.[27] have investigated the relationship between x-ray density and the composition for the C23H48/C25H52 system. Densities of the mixtures are found to be lower than those of pure components. They have interpreted the decrease in the density of the mixtures as due to the presence of vacancies. According to these results, the chain conformational disorder in the C30H62/C36H74 mixture would be located near chain end regions and the chain interior is unaffected. Interior chain kinks may hardly play a role in the change of the integrated intensity at low-temperature. For present work, the variation of the integrated intensity with composition at room temperature could be a measure of the change in disorder arising from the chain length mismatch as well as corresponding bulk density of the mixture. At higher temperature, there are several possibilities leading to increase in the integrated intensity. As mentioned previously, the longitudinal disorder, coupled with the formation of kinks, could be predominate.

The present data indicate imperfections generated at high-temperature can result in an extension of the interfacial region. In this region, the electron density smoothly declines in going away the perfect portion of a lamella to chain end regions. The increased integrated intensity at higher temperature implies greater electron density deficiency at interfacial regions, hence increased looseness of the structure. The analysis of the electron density directly shows the temperature dependence of the extension of the interfacial region (i.e. an electron density deficiency region) from the fact that the interfacial thickness, and the total electron density deficiency of the interfacial region with respect to the density of well-ordered portion of a lamella, increase with increasing temperature. For a pure paraffin, Basson and Reynhardt[28] have recently found the
energy difference between all-trans and gauche bonds is about 10-14KJ/mol and seems to
decrease with an increase in chain length. The decrease in the long spacing of longer
chains (C_{36}H_{74} and C_{40}H_{82}) at high-temperature also indicates that the disorder of a longer
chain is easier than that of a shorter chain. However, for a paraffin mixture, the situation
is quite different. Snyder et al [24-25] found that the concentration of end-gauche bonds in
the C_{46}/C_{50} mixture is significantly larger than that of C_{19}/C_{21}. For the C_{46}/C_{50} mixture,
the sum of gauche concentrations at bond positions 2 and 3 is found to be about 2.5 times
greater than that for C_{19}/C_{21}. More important, the concentration of gauche bonds at the 3
position is also greater for C_{46}/C_{50} mixture. A very important conclusion drawn from
these results is that the more bond positions are disordered if the chain length mismatch is
greater, and that change in absolute chain length does not play an important role. The
greater chain length mismatch in the C_{30}H_{62}/C_{36}H_{74} mixture is an essential reason for the
extension of the interfacial region at high-temperature. Since there is a length difference
of 6 bonds between the two kinds of chains in the C_{30}H_{62}/C_{36}H_{74} mixture, bonds up to 4
and 5 positions from ends of longer chains could be disordered. There would be more
disorder on the C_{36}H_{74} chains than on the C_{30}H_{62} chains.

The variation of the paracrystalline distortion g with the composition and temperature
would be related to this conformational disorder on the longer chain component. Figure(3.34) schematically shows possible packing conformations in chain end regions for
a 1:1 mixture. In constructing the schemes, only one lamella is displayed and possible
kinks along longer chains are not shown for clarity. It is assumed that the chain packing
is arranged as close as possible between adjacent lamellae so as to minimize vacancies. In
case a, there is a correlation in the longitudinal orientation between lamellae because the
chain-length ‘averaging’ is accomplished by the interleaving of chains at lamellar
surfaces. This conformational arrangement should correspond to a larger statistical
fluctuation of lamellae and therefore a larger value of the paracrystalline distortion g.
Hosemann et al[29] first stated that this correlation exists in pure paraffins. In case b,
lamellae are not correlated at all so that the g value may approach zero. These two
packings are extreme arrangements. The actual structure is of course located somewhere
between these two extremes, depending on the composition and temperature. As seen
earlier, the paracrystalline distortion g at room temperature increases by mixing and is at
its maximum around 40% C_{36}H_{74}. This result indicates that the interlayer correlations that
characterize structures are at their maximum around 40% longer chains. In this case, there would be a number of vacancies around chain end regions at lamellar surfaces, which results in a greater contrast of the electron density and therefore a maximum scattered intensity. In the case of very dilute C_{36}H_{74} in C_{30}H_{62}, two possibilities are shown in (a) of figure(3.35). All chains have been shortened to one-third for simplicity. The g value in this case arises from statistical fluctuation mainly with respect to shorter chains, C_{30}H_{62}. However, the types of the statistical fluctuation depend on longer chains. Structure i is preferred due to a smaller g value. Because end-gauche C_{36}H_{74} chains occur, the correlation in the longitudinal direction is decreased and statistic fluctuation is therefore reduced. In the case of very dilute C_{30}H_{62} in C_{36}H_{74}, as shown in (b) of figure(3.35), the g value relates to statistical fluctuation with respect to the longer chains, C_{36}H_{74}. The disorder of longer chains has a low probability of occurring due to higher energy required[28]. The shorter chain action can not influence the g value. Even if few longer chains fill 'holes' created by isolated shorter chains, as shown in ii case of (b) of figure(3.35), the g value is not expected to significantly change. In this case, the behavior of statistical fluctuation in a C_{30}H_{62}/C_{36}H_{74} lamella is similar to that in a pure C_{36}H_{74}, and the g value is also smaller. However, as seen from the above discussions, the reasons why there is a smaller g value both in case (a) and case (b) are different.

The temperature dependence of g indicates that the concentration of the gauche-bond should increase with increasing temperature. At high temperature, the formation of more gauche-bonds on longer chains causes a continuous reduction in the statistical fluctuation. This result can be related to the extension of the interfacial region. This result is also qualitatively consistent with the vibrational spectroscopic studies of Snyder et al[24-25].
Chapter 3 Studies of Paraffin Mixtures by SAXS

C\textsubscript{36}H\textsubscript{74} very dilute in C\textsubscript{30}H\textsubscript{62}  C\textsubscript{30}H\textsubscript{62} very dilute in C\textsubscript{36}H\textsubscript{74}

Figure (3.35) Possible packing schemes for (a) C\textsubscript{36}H\textsubscript{74} dilute in C\textsubscript{30}H\textsubscript{62} and (b) C\textsubscript{30}H\textsubscript{62} dilute in C\textsubscript{36}H\textsubscript{74}. Chains are shortened to one-third for clarity.

All-Trans  End-Gauche  Kink  Double-Gauche
\text{t}_{14} \quad \text{gt}_{13} \quad \text{t}_{6}\text{gtg}'\text{t}_{5} \quad \text{gg}\text{t}_{12}

Figure (3.36) Examples of a number of defects that occur in paraffins, illustrated for C\textsubscript{17}H\textsubscript{36} [ref. 30].

The conformational disorder can be present end-gauche(gt\textsubscript{\mu-1}), double gauche (gg\textsubscript{\mu-2}), and kinks (t\textsubscript{\mu}e\textsubscript{gtg}'t_{\mu-3})[30], as shown in figure (3.36) for C\textsubscript{17}H\textsubscript{36}. In this notation \mu is the number of intermethylene C-C bonds and g and g' here denote rotations about the relevant C-C bond through 120° and -120°, respectively. The total number of carbon atoms per chain is \mu + 3.

The above discussions on the disorder distribution of paraffins and their mixtures may not be extended simply to the case of polyethylene or long chain paraffins. The quite
different nature of lamellar structure in long chain polyethylene distinguish its morphology. We here make some comparisons of the different behavior of temperature variation of the paracrystalline distortions for short chain paraffins and long chain polyethylene.

Figure (3.37) schematically shows typical models of lamellar structures for polyethylene (a, b) and long chain paraffin (c, d) [31]. We take the case a as an example for discussion. Since a lamella is constituted by a single or a folded chain, any movement of a segment may affect neighboring segments and even whole lamellae. The change in the paracrystalline distortion should therefore involve rearrangement of lamellae. It is very difficult to draw this rearrangement, however. The forward movement of a segment in order to fill a 'hole' unavoidably creates a new one in another end of the segment, which can not change the statistical fluctuation. On the other hand, so called chain end effect, for example, the formation of the end-gauche bond, is not accepted. The paracrystalline distortion independence of the temperature in the polyethylene could be due to this reason.

As already suggested by Krenzer and Ruland [32], the most probable origin of the microstrain distribution in the case of semi-crystalline polyethylene is the difference in thermal expansion coefficients of crystalline and amorphous domains. The thermal expansion coefficient of amorphous domains is expected to be larger than that of crystalline domains. As a result, the microstrain is compression in crystalline domains and extension in amorphous domains. For C_{30}H_{62}/C_{36}H_{74} mixtures, it is obvious that the most probable origin of the microstrain distribution would be the thermal expansion
coefficients of the crystalline region and vacancies. The thermal expansion coefficient of vacancies is larger than that of the crystalline regions. The microstrain can also yield a strong correlation between distance variations of a sequence of net planes in the vicinity of defects\[32\]. The microstrain occurring in C\(_{30}\)H\(_{62}\)/C\(_{36}\)H\(_{74}\) mixtures is mainly due to the chain length mismatch and conformational disorder. Thus, at room temperature the microstrain is expected to concentrate near chain end regions due to a number of vacancies there. The maximum microstrain implies maximum interlayer correlations. This result is consistent with the results obtained from the integrated intensity and paracrystalline analysis.

In the investigation of the relation between the microstrain and temperature in the polyethylene, the microstrain was found to decrease with increasing temperature\[32\]. One of the reasons for this behavior may be due to a thickening (or ordering) of existing crystallite at the expense of the intervening amorphous region. Another reason may be related to a decrease in thermal expansion coefficient difference at high-temperature. In C\(_{30}\)H\(_{62}\)/C\(_{36}\)H\(_{74}\) mixtures, the situation may be quite different, however. Vacancies would be introduced due to the longitudinal disorder and kinks relating to the formation of the gauche-bond at high-temperature. The decrease in the microstrain may therefore be compensated. On the other hand, some of the vacancies in chain end regions could be annihilated due to the longitudinal migration of molecules with end-gauche bond. This translation could minimize the vacancy volume in chain end regions and lead to a decrease in the microstrain. The fact that the microstrain basically does not change in the range of the measured temperature would be a balance consequence of all effects mentioned. The experimental data indicate vacancies generated in interfacial regions should be more than those annihilated in chain end regions. At high temperature, the microstrain distribution is also not uniform within lamellae but concentrated in interfacial regions. The distribution profile of the microstrain in the interfacial region would decline smoothly away from the chain end regions to the perfect portion of lamellae. The inhomogeneous distribution of the microstrain can cause a curvature in the plot of \(<E^2>^{1/2}\) versus \(\xi\). The narrower line width of half height of the peak at high-temperature, as seen in figure\(3.3\), is an effect of inherent microstrain\[32\].
The above procedure involves a rearrangement of lamellar structure and is therefore associated with changes in the density profile. These changes include a decrease in the length of the well-ordered portion and increase in the poorly-ordered portion (or the interfacial region) in lamellae. Figure (3.38) schematically shows density changes in lamellae at lower and higher temperatures.

Figure (3.38) Electronic density profiles of C$_{30}$H$_{62}$/C$_{36}$H$_{74}$ mixtures at (a) low-temperature and (b) high-temperature.

3.6 CONCLUSIONS

Small angle x-ray scattering measurements on binary C$_{30}$H$_{62}$/C$_{36}$H$_{74}$ mixtures as a function of composition and temperature show characteristics consistent with the results of Snyder et al [24-25]. Conclusions drawn from the experiments are as follows:

(1) For C$_{36}$H$_{62}$/C$_{36}$H$_{74}$ mixtures, the paracrystalline distortion and microstrain are dependent on the composition. They increase to a maximum in the range from 40% to 60% of the C$_{36}$H$_{74}$ component.

(2) The paracrystalline distortion is found to decrease with increasing temperature while a temperature independence of the microstrain is observed.

(3) The paracrystalline distortion and microstrain, combined with the integrated intensity,
can relate to the conformational disorder and its distribution.

(4) The interfacial regions in lamellae are caused by the conformational disorder. The interfacial thickness increases with increasing temperature in the range of the experimental temperature.

D. D. Derksen, Macromolecules 2, 135 (1969)


R. E. Warren, Acta Cryst. 8, 483 (1955)


M. A. Bushman, R. L. McCullough, and R. L. Miller, Acta Cryst. 9, 100 (1956)

M. E. Bertaut, Comptes Rendus 258, 485 (1964)


A. P. Czerski, I. De Nicolò, and J. Descot, Phys. Rev. 135, A156 (1964)

D. L. Derksen, Macromolecules 16, 2962 (1983)


R. L. Warren, Prig. Metal Phys. 4, 137 (1959)


S. Blashey and W. Porstendorf, Real. Acta 4, 174 (1964)
Chapter 3  Studies of Paraffin Mixtures by SAXS

3.7 REFERENCES

2. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Press, Pittsburgh, Pa., 1953
5. B. E. Warren, Acta Cryst. 8, 483 (1955)
7. R. Bonart, R. Hosemann, and R.L. McCullough, Polymer 4, 199 (1963)
10. M. F. Bertaut, Comptes Rendus 228, 492 (1949)
20. B. E. Warren, Prog. Metal Phys. 8, 147 (1959)
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4.2 EXPERIMENTAL DETAILS

Crucible samples of pure paraflins, C12H26, C16H34, and C20H42, were heated in unlabeled samples were obtained from Saphic (Belgium, 1977). The partially saponified and the corresponding unsaponified samples were obtained from Miltex, Quebec, Canada. The dried samples had a moisture content not exceeding a maximum concentration of 0.35. This moisture content may be of the crystalline structure, which are in better order than in the same with a different concentration spectra in solution scattering experiments. The experiments were performed over two days in the unit before freezing. The frozen samples were investigated in several concentrations. The samples were subjected to long-term storage and subjection to temperatures above six to seven months. Figures 1.1 show the C12H26, C16H34, and C20H42 mixture. The orientation and spinning investigations of the freezing process were within the detection level of the
CHAPTER FOUR  STUDIES OF BINARY PARAFFIN MIXTURES
BY SMALL ANGLE NEUTRON SCATTERING

4.1 INTRODUCTION

In this chapter we will investigate binary paraffin mixtures by using small angle neutron scattering. A fully deuterated sample as one component has been used to enhance the scattering contrast. Experimental details are given. The results concern the demixing and the structural arrangements of two components as well as the morphology transition between commensurate and incommensurate solids. These results provide information complementary to those obtained by other techniques [1,2] and answer some as yet unresolved questions [3,4].

4.2 EXPERIMENTAL DETAILS

C30/C36 binary paraffin pairs, C_{30}H_{62}/C_{36}D_{74} and C_{30}D_{62}/C_{36}H_{74}, were investigated. The unlabeled hydrocarbons were obtained from Supelco (Bellefonte, PA, USA) with the purity grade > 99.5% and the corresponding deuterated analogous from MDS Isotopes (Montreal, Quebec, Canada). The deuterated samples had a manufacturer's specification indicating a deuterium concentration > 99.0%. The mixtures, on mole/mole basis, were made of the crystalline hydrocarbons which were melted together in an inert atmosphere in the same silica ultraviolet absorption spectroscopy cells used for the subsequent neutron scattering experiments. The components were left to interdiffuse for a period of one to two days in the melt before cooling. The dynamics of demixing process were investigated at several temperatures. The neutron scattering was generally measured at one hour intervals subsequent to quenching. Ageing times of samples at room temperature were about six or twelve months. Figure 4.2.1 shows the phase diagram of the C_{30}H_{62}/C_{36}D_{74} mixture [5]. The compositions and quenching temperatures in the investigation of demixing process were within the demixing region of the phase diagram.
Small Angle Diffractometer (SAD) at the Intense Pulsed Neutron Source, Argonne National Laboratory, which uses wavelengths in the range 2<\lambda^{-1}<14, was used for the neutron scattering measurements. The details of the instrument have been given in Chapter 2.

4.3 PRELIMINARY DATA REDUCTION

The methods of the elimination of incoherent scattering for SANS have been reviewed in Chapter 2. Figure (4.3.1) shows a representative plot of \( I(Q)^4 \) versus \( Q^4 \). The slope of the least-squares fit of data at higher \( Q \) yields a amount of background scattering to be subtracted. All data were treated in the same way. It should be noted that this method is approximate in that there must be a small contribution to the magnitude of the slope arising from coherent scattering. However, this overcorrection represents only a small fraction of the total scattering and is within the experimental uncertainties of measurements. Figures (4.3.2) and (4.3.3) show representative scattering patterns after
Figure (4.3.1) The plot of IQ^4 versus Q^4 of SANS data obtained for the 1:4 C_{30}H_{62}/C_{36}D_{74} mixture. The slope of least-squares fit of data at higher Q yields an amount of background scattering to be subtracted.

Figure (4.3.2) Representative plots of the intensity (plotted in a way of IQ^2) versus wavevector Q for the 3:8 C_{30}H_{62}/C_{36}D_{74} mixture quickly quenched from the melt to room temperature, aged for a long time, and then slowly heated to higher temperatures.

background correction. Two significant points should be noted. Firstly, when referring to the scattered intensity I(Q,t), we imply that the incoherent scattering has been subtracted from the observed scattered intensity in the way discussed in Chapter 2. Secondly, the scattered intensity has been calibrated in absolute units by comparison with the scattering from a standard sample.
Chapter 4  Studies of Binary Paraffin Mixtures by SANS

4.4 RESULTS

Experimental results of $C_{30}H_{62}/C_{36}D_{74}$ and $C_{30}D_{62}/C_{36}H_{74}$ are reported. The section is arranged according to experimental conditions. Although more detailed discussion of results will be given later, some unavoidable discussion is immediately involved in order to establish a general physical picture and initial understanding of present system.

4.4.1 TIME EVOLUTION OF SCATTERING PATTERNS

First, we report the results obtained from $C_{30}H_{62}/C_{36}D_{74}$ mixtures which were rapidly quenched from the melt to chosen temperatures. SANS data collected at different times after quenching at these temperatures derive from the demixing process. The 1:1 and 1:4 mixtures are taken as examples.

Figure(4.4.1.1) shows typical scattering patterns obtained from the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture, which is compositionally symmetric, quickly quenched to 20°C, 25°C, and 60°C. Each scattering curve was accumulated for one hour at 20°C and 25°C, and for two hours at 60°C. The mixture shows new SANS patterns which are quite different from the...
Figure (4.4.1.1) Plots of the scattered intensity versus wavevector for the 1:1 $\text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74}$ mixture quickly quenched from the melt to chosen temperatures.
patterns expected for the two original components. At 20°C and 25°C, a marked hump in each scattering pattern starts to appear at the earlier times and develops to a distinct maximum at a certain Q value at the later times. As the annealing time increases, the maximum becomes more prominent and the peak shape becomes narrower. The results indicate that after rapid quenching, the lamellar structure created in a very early stage is disordered and probably contains a broad distribution of lamellar spacings, and the structure becomes sufficiently ordered in the later stages as to produce a marked Bragg reflection peak. The application of Bragg’s law to the peak gives the long spacing. It is noteworthy that the scattered intensity at 25°C is somewhat larger than that at 20°C on the same time scale. At 60°C, the scattering patterns are found to be independent of annealing time and no information of lamellar structure and structural change is observed. The data show that the mixture forms a intrinsic separation structure of lamellae at lower temperatures or is solid solution at the higher temperature and indicate an optimum temperature for annealing in the new lamellar structure between 20°C and 60°C.

Figure(4.4.1.2) shows typical scattering patterns for the 1:4 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture which is significantly unbalanced in concentration. A very different feature between figures(4.4.1.1) and (4.4.1.2) is observed. A noticeable difference is that the scattering patterns of the 1:4 mixture at first sight displays no hump. Inserts in figure(4.4.1.2) are enlarged parts of scattering patterns in which the very weak and broad diffraction peaks can be seen at 41°C, very blurred at 33°C and 30°C, and can not be indicated at 26°C. The direct application of Bragg’s law to peaks may result in larger incorrect long spacings. More correct long spacings can be obtained from the scattering patterns plotted in a way of \( IQ^2 \) versus Q. As shown in figure(4.4.1.3), two distinct maxima appear at annealing temperatures of 41°C, 33°C, and 30°C. Both distinct maxima look like some sort of average of the Bragg reflections in the mixture. However, the mixture would actually be separated lamellae which are primarily \( \text{C}_{30}\text{H}_{62} \) or \( \text{C}_{36}\text{D}_{74} \). The scattering patterns indicate that the average size of \( \text{C}_{30}\text{H}_{62} \) clusters in the 1:4 mixture may be smaller than that in the 1:1 mixture. It is noted that these scattering patterns are very similar to those of mixtures of high density polyethylene and low density polyethylene[6,7], and are generally seen in systems with a high degree of the crystallinity or in systems with a narrow distribution of crystalline and amorphous[8]. For mixtures of high density polyethylene and low density
polyethylene, the scattering patterns were explained as a segregation of bundles of lamellae, which are primarily high density polyethylene and low density polyethylene[6,7]. For the 1:4 mixture, the peak position at 26°C is not pronounced. We also note that the scattered intensity is stronger at higher temperatures and that the first peak shift to higher Q with increasing quenching temperature. This feature is related to differences in the average cluster size and the demixing rate. Our measurements suggest that between room temperature and 41°C, the average cluster size and demixing rate could increase with increasing temperature and reach a maximum near 41°C. Generally speaking, at low temperature, the crystallization of the higher melting component is faster and the diffusion of lower melting component is slower, so the degree of segregation is
Figure (4.4.1.3) Representative plots of the intensity (plotted in a way of IQ^2) versus wavevector Q for the 1:4 \( C_{30}H_{62} / C_{36}D_{74} \) mixture quickly quenched from the melt to chosen temperatures.

lower. However, at high temperature, the diffusion is faster and crystallization is slower, so the degree of segregation is higher. The quantitative analysis will be given.

4.4.2 LONG TIME AGEING EFFECTS ON SCATTERING PATTERNS

Effects of the ageing time on scattering patterns have been investigated. From figures (4.4.2.1) to (4.4.2.3), the scattering patterns obtained from several mixtures at different ageing times after quenching are presented. The ageing behavior of the mixtures can be summarized as follows: (1) the scattered intensity increases with ageing time, (2) the peak shape becomes the narrower with ageing time, and (3) the peak position shifts slightly to the smaller Q with ageing time. These results suggest qualitatively that in evolution from initial arrangement of an solid solution to a well-defined incommensurate structure, the growth of the fractionated solid takes a very long time at room temperature although the fractionation in quenched samples is almost instantaneous after quenching.
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Figure (4.4.2.1) The intensity (plotted in a way of $I Q^2$) versus wavevector $Q$ for the 3:8 $C_{36}H_{62}/C_{36}D_{74}$ quenched from the melt and aged at room temperature. Filled triangles and open squares represent 750 min and about six months.

Figure (4.4.2.2) The intensity (plotted in a way of $I Q^2$) versus wavevector for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture quenched from the melt and aged at room temperature. Filled triangles and open squares represent 630 min and about six months.

It is noted that weak reflections are observed at higher $Q$. Taking aged 3:8 $C_{30}H_{62}/C_{36}D_{74}$ as an example, the origin of these weak reflections is examined. It is found that the $Q$ values of these peaks are 2 and 3 times larger than that of the dominant peak. Therefore, these weak reflections may be the second ($Q=0.136\AA^{-1}$) and the third ($Q=0.21\AA^{-1}$) maxima of the first order ($Q=0.072\AA^{-1}$). Similar results are also found for 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture. The positions of higher $Q$ reflections for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture are difficult to locate, however. Although, as seen later, a peak near $Q=0.136\AA^{-1}$ is also observed in pure $C_{36}D_{74}$ aged for a short time, it does not exist after long time ageing. We note that the position of the second maximum is very close to that of long spacing of pure $C_{36}D_{74}$.
Chapter 4  Studies of Binary Paraffin Mixtures by SANS

Figure (4.4.2.3) The intensity (plotted in a way of $I Q^2$) versus wavevector for the 1:1 $C_{36}H_{62}/C_{36}D_{74}$ mixture quenched from the melt and aged at room temperature. Filled triangles and open squares represent 630 min and about six months.

Figure (4.4.2.4) The intensity (plotted in a way of $I Q^2$) versus wavevector for the 4.3:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture quenched from the melt and aged at room temperature for about six months (open squares). Filled squares represent scattered intensity obtained from about one day standing at room temperature after slow cooling.

Figure (4.4.2.4) shows a comparison of the scattering pattern (plotted in a way of $I Q^2$) for the 4.3:1 $C_{30}H_{62}/C_{36}D_{74}$ quickly quenched from the melt and aged at room temperature for about six months with that obtained from one day ageing sample after slow cooling from the melt. The scattering pattern of the aged sample shows the feature of microphase separation, as seen in other quenching samples, while no evidence of the microphase separation for the sample aged only one day after slow cooling is observed. The effect of the ageing time on the separation of $C_{30}H_{62}/C_{36}H_{74}$ mixtures after slow cooling was observed by Dorset[1-2] using differential scanning calorimetry (DSC). It was found that $C_{30}H_{62}/C_{36}H_{74}$ mixtures formed by slow cooling from the melt slowly fractionated into an
incommensurate solid solution after about two days standing at room temperature[1-2]. The DSC showed a small composition independent endotherm near 51°C, which was taken as an evidence for the transition temperature from a solid solution to a fractionated solid for C₃₀H₆₂/C₃₆H₇₄[1-2]. The SANS data here agree and show that in contrast to rapid quenching, no fractionation occurs in C₃₀H₆₂/C₃₆D₇₄ mixtures aged one day after slow cooling from the melt.

4.4.3 VARIATION OF SCATTERING PATTERNS WITH TEMPERATURE

In another series of experiments, long time aged samples were slowly heated from room temperature to the melt. In this way SANS data allow us to establish the extent of variation of fractionated solids with temperature and to determine the mixed-demixed transition temperatures in C₃₀H₆₂/C₃₆D₇₄. As examples, figures (4.4.3.1) and (4.4.3.3) show the temperature dependence of SANS patterns measured for 1:1 and 1:4 C₃₀H₆₂/C₃₆D₇₄. In order to clearly see the variation of peaks with temperature, the scattering patterns plotted in a way of IQ² are also shown. As seen, the peaks of the microphase separation begin to decrease in the scattered intensity as the temperature is raised up to a certain extent. It is noted that as a specific temperature is approached the scattering patterns show sudden change: the scattered intensity dramatically decreases and then the peak disappears.

Figure (4.4.3.1) The variation of experimental scattered intensity with temperature for the 1:1 C₃₀H₆₂/C₃₆D₇₄ mixture.
Figure 4.4.3.2 The scattering patterns (plotted in a way of $IQ^2$) of figure 4.4.3.1

Figure 4.4.3.3 The variation of experimental intensity (left) and $IQ^2$ (right) with temperature for the 1:4 $C_{36}H_{62}/C_{36}D_{74}$ mixture.
4.4.4 SCATTERING PATTERNS OF TWO PHASE DISSOLUTION

Scattering patterns for aged mixtures quickly heated from a temperature to the another were also collected. Figure (4.4.4.1) shows log-log plots of scattering patterns for the 1:4 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) quickly heated from room temperature to 46°C. Figure (4.4.4.2) shows the scattering patterns plotted in a way of \( IQ^2 \) for the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) quickly heated to chosen temperatures. The results indicate a dissolution of fractionated solids.

![Figure (4.4.4.1) Log-log plots of the scattered intensity versus wavevector for aged 1:4 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) quickly heated from room temperature to 46°C.](image1)

![Figure (4.4.4.2) The scattering patterns plotted in a way of \( IQ^2 \) for aged 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) quickly heated to chosen temperatures.](image2)

4.4.5 SCATTERING PATTERNS OF A \( \text{C}_{36}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) MIXTURE

Our experiments were also extended to the 1:1 \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) mixture, the reverse pair of the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \). In this mixture the molar ratio of \( D \) to \( H \) is different, as is the difference in melting points and chain volumes between two pure components. SANS scattering patterns obtained from the \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) mixture allow us to investigate isotope effects on the demixing process and morphological arrangement.
Figure (4.4.5.1) Comparisons of the time evolution of scattered intensities obtained from the 1:1 C_{30}H_{62}/C_{36}D_{74} (filled triangle) and its reverse pair 1:1 C_{30}D_{62}/C_{36}H_{74} (cross) quenched from the melt to 20°C.

Figure (4.4.5.2) The scattering patterns (plotted in a way of IQ^2) of figure (4.4.5.1)
Figure (4.4.5.3) The difference in the scattered intensity between 1:1 $C_{30}H_{62}/C_{36}D_{74}$ and 1:1 $C_{36}D_{62}/C_{36}H_{74}$ mixtures quenched from the melt to 20°C as a function of annealing time at $Q=0.082\text{Å}^{-1}$.

In figure (4.4.5.1), the scattering patterns of the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ and the corresponding reverse pair 1:1 $C_{30}D_{62}/C_{36}H_{74}$ at subsequent times after quenching from the melt to 20°C are compared. The annealing time is the same for each case. The scattering patterns plotted in a way of $IQ^2$ are also shown in figure (4.4.5.2). The results apparently indicate that the demixing and therefore the lamellar distribution of 1:1 $C_{30}H_{62}/C_{36}D_{74}$ and 1:1 $C_{30}D_{62}/C_{36}H_{74}$ have quite different behavior. First, the weak hump related to the microphase separation in the scattering pattern of the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture at the first hour develops into a pronounced peak at 14 hours in the $Q$ range from 0.07 to 0.08Å$^{-1}$ but for the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ only a weak and broad feature, at approximately same $Q$ value, is detectable after the same elapsed time. At any given time, it is found that the scattered intensity of the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ is always weaker than that of the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ in the $Q$ range from 0.06 to 0.12Å$^{-1}$. What is more, the difference in the scattered intensity in this $Q$ range increases as annealing time elapses within the time scale of the experiments. The plot of this difference at $Q=0.082\text{Å}^{-1}$ as a function of annealing time is shown in figure (4.4.5.3), which indicates the time required to reach an equilibrium state for the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ may be shorter than that for the 1:1 $C_{30}H_{62}/C_{36}D_{74}$. Second, in contrast to the microphase separation peak around $Q=0.082\text{Å}^{-1}$, a peak at $Q=0.136\text{Å}^{-1}$ corresponding to the structure expected for enriched pure $C_{36}H_{74}$ is found to be much stronger in the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ than that in the 1:1 $C_{30}H_{62}/C_{36}D_{74}$. Third, though this is easily overlooked, the scattered intensity of the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ in the lowest accessible $Q$ range is stronger than that of the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ at the same annealing time. The results suggest that the structural arrangement and rate of whole demixing process in $C30/C36$ pairs would be quite different due to the isotope effects.
Figure (4.4.5.4) The variation of the intensity (plotted in a way of IQ^2) with temperature for the 1:1 C_{30}D_{62}/C_{36}H_{74} quenched from the melt to room temperature, aged for about six months, and then slowly heated to the melt.

Figure (4.4.5.4) shows the variation of the intensity plotted in a way of IQ^2 with temperature for the 1:1 C_{30}D_{62}/C_{36}H_{74}. Although there are similarities between 1:1 C_{30}D_{62}/C_{36}H_{74} and 1:1 C_{30}H_{62}/C_{36}D_{74} mixtures, obvious differences are observed. A noticeable difference is that the peaks at Q=0.07Å^{-1} and Q=0.136Å^{-1} do not simultaneously disappear. Instead, a two-stage process of lamellar dissolution is observed. The peak at Q=0.07Å^{-1} disappears with increase in temperature, similar to the dissolution of the 1:1
Figure 4.4.5.5 A comparison of second peaks obtained from figure 4.4.5.4 at room temperature (open squares) and 60°C (filled triangles).

\[ C_{30}H_{62}/C_{36}D_{74} \]. However, it can be clearly seen that the peak at \( Q=0.136\text{Å}^{-1} \) hardly changes its scattered intensity until about 65°C. Above this temperature, the scattered intensity rapidly decreases so that it is barely visible near 75°C and gone completely by 80°C. It is found that the peak position \( Q=0.136\text{Å}^{-1} \) at room temperature is slightly decreased to \( Q=0.134\text{Å}^{-1} \), which is very close to that expected for the long spacing of pure \( C_{36}H_{74} \), at higher temperatures, for example, at 60°C. The more important we observe is that the shape of the second peak becomes narrower and valley between the first and second peaks becomes higher when the temperature is raised up to some extent, as shown in figure 4.4.5.5. Again, the temperature dependence of scattering pattern indicate that the lamellar distribution in the 1:1 \( C_{30}D_{62}/C_{36}H_{74} \) mixture very differs from that in the 1:1 \( C_{30}H_{62}/C_{36}D_{74} \).

Figure 4.4.5.6 shows a comparison for the effect of ageing time on the scattering pattern of the 1:1 \( C_{30}D_{62}/C_{36}H_{74} \). It is interesting to note that the scattering pattern around the first peak develops to a sharp peak similar to that of the 1:1 \( C_{30}H_{62}/C_{36}D_{74} \) after long time ageing. The long spacing corresponding to separated lamellae changes from 75Å at 870 minutes to 95Å after about six month ageing. The peak position and shape of the second peak do not have significantly change before and after long time ageing. Although the statistics of counting limit accuracy here, the peak near \( 0.21\text{Å}^{-1} \) is still detectable. The results are presented for the unexpected effect of long time ageing, which shows that the structural rearrangement and therefore the molecular migration.
Figure (4.4.5.6) $Q^2$ versus $Q$ for the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ mixture quenched from the melt to 20°C, and aged for 870 min (filled triangles) and for about six months (open squares). The enlarged peaks at $Q=0.136\text{Å}^{-1}$ are shown in (b).

4.4.6 SCATTERING PATTERNS OF PURE PARAFFINS

Figure (4.4.6.1) shows plots of $Q^2$ versus $Q$ for pure $C_{36}D_{74}$. Part (a) of the figure shows data for the sample aged several days after quenching and then heated to temperatures 25°C ≤ T ≤ 45°C while part (b) refers to temperatures 47.5°C ≤ T ≤ 70°C. Part (c) of the figure shows scattering pattern for pure $C_{36}D_{74}$ aged at room temperature for a long time after quenching. The long spacings obtained from the first peaks of (a), (b), and (c) are 51.5Å, 50Å, and 47.5Å within the uncertainty of the experiments. The long spacings obtained from (a) and (b) are not equilibrium and correspond to a complicated situation of boundaries between lamellae. The long spacing obtained from (c) is an equilibrium value.
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Figure (4.4.6.1) The intensity (plotted in a way of IQ^2) versus Q for pure C_{36}D_{74}.

Figure (4.4.6.2) The intensity plotted in a way of IQ^2 versus Q for pure C_{39}H_{62}.

The long spacings obtained from the second peaks of parts (a) and (c) are about 43Å related to monoclinic phase. It is found that the monoclinic phase gradually decreases and may disappear as temperature is raised to a certain extent. We also note that no monoclinic phase is detectable for the sample undergoing a long time ageing, as seen in part (c) of figure (4.4.6.1). When the sample was aged for a short time, a peak near Q=0.21Å⁻¹ is
observed but it disappears after a long time ageing. Figure (4.4.6.2) shows a plot of IQ$^2$ versus Q for pure C$_{30}$H$_{62}$. As seen the information is dramatically reduced.

4.5 DISCUSSION

4.5.1 MIXED-DEMIXED TRANSITION OF C30/C36 PAIRS

Studies of the phase behavior of polymers or oligomers undergoing crystallization have been an important subject. For example, the phase behavior of paraffin binary mixtures, as a model for the polydisperse polymethylene chain packings found in polyethylene lamellae, have received considerable attention for many years. For certain binary paraffin mixtures, the chain length difference between the two components determines whether segregation occurs and how fast the segregation is [1,2,5,9]. Dorset has reported [1-2] a redetermination of the phase diagram for C$_{30}$H$_{62}$/C$_{36}$H$_{74}$ by using differential scanning calorimetry and electron microscopy. Snyder et al [5] have recently constructed a more detailed phase diagram for the C$_{30}$H$_{62}$/C$_{36}$D$_{74}$ mixtures. The DSC data showed [1,2] that after several days standing (about 2 days) at room temperature after slow cooling from the melt, the C$_{30}$H$_{62}$/C$_{36}$H$_{74}$ mixtures slowly fractionated and the transition temperature from a solid solution to a fractionated solid was near 51°C, independent of the composition. There has been an increased interest in isotopic mixtures. Stehling et al [10] first reported the phase diagrams of mixtures of paraffin and deuterated paraffin as well as polyethylene and deuterated polyethylene. They demonstrated different melting temperatures (about 4°C) between deuterated and normal polyethylene. These findings were followed by reports of segregation of mixture of C$_{36}$H$_{74}$/C$_{36}$D$_{74}$ during the solidification from melt [11]. Later, Krimm and Ching [12] investigated the phase behavior of a ternary system, polyethylene/deuteropolyethylene/benzene. The conclusion emerged from their work is that finite compositional segregation exists, which is due to isotope effects, but segregation only becomes significant at intermediate concentration. Spells and Sadler [13] have reported that there is no neutron scattering evidence for segregation in the 1:9 C$_{32}$H$_{66}$/C$_{32}$D$_{66}$ mixture and the molecules are randomly arranged within the crystal. Wu and Wignall [14-15] have investigated SANS of partially segregated blends of polyethylene and deuteropolyethylene in terms of the geometric arrangement of molecules. They have demonstrated that at very low concentrations of the segregation, random phase

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approximation theory is applicable. English et al [16] analyzed DSC data from mixtures of PEH/PED and $C_{36}H_{74}/C_{36}D_{74}$. From their point of view, the origin of phase segregation in PEH/PED mixtures as deduced from the neutron scattering experiments is not predominantly due to isotope effects but probably reflects differences in molecular weight distribution, the degree of branching, or perhaps the presence of voids. Dorset [17] has recently studied solid solutions composed of perdeuterated paraffins and their hydrogenated analogous with identical chain lengths. It was found that perdeuterated paraffins have quite similar structure properties to paraffins with equal chain length. Binary phase diagrams were reported to be ideal for the phase boundary between the rotator phase and the melt, and for the orthorhombic to rotator transition.

From our data, the transition temperature of $C_{30}H_{62}/C_{36}D_{74}$ mixtures can be precisely determined by measuring the differential scattered intensity $dI(Q,T)/dT$ as a function of temperature $T$. Transition points are determined from turning points in plots of $dI(Q,T)/dT$ versus $T$. The samples were first quenched from the melt to room temperature, and then aged for a long time before use. Aged samples, which are considered to be well-separated two-phase mixtures, were heated at very slow rates from room temperature to the melt. The data obtained in this way indicate the boundary between a solid solution and a fractionated solid. When comparing $C_{30}H_{62}/C_{36}D_{74}$ in this

![Figure(4.5.1.1) Plots of dI(Q,T)/dT as a function of temperature for the 1:4 C_{30}H_{62}/C_{36}D_{74} mixture at rates of 0.14°C/min and 0.4°C/min.](image)
Figure 4.5.1.2 Plots of $\frac{dI(Q,T)}{dT}$ as a function of temperature for the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture at rates of 0.14°C/min and 0.4°C/min.

Work with $C_{30}H_{62}/C_{36}H_{74}$ in the literature[1], the isotope effects and differences in sample treatments should be taken account.

Figures [4.5.1.1] and [4.5.1.2] show SANS heating curves recorded at two heating rates for 1:4 and 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixtures, respectively. The feature of these traces is quite similar to that of the endotherm-temperature curves in the differential scanning calorimetry (DSC). The observation indicates that the effect of heating rate used on transition points is within the experimental errors.

From SANS patterns and DSC data in the literature[1,2], no evidence was given for the demixing in $C_{30}H_{62}/C_{36}D_{74}$ and $C_{30}H_{62}/C_{36}H_{74}$ mixtures which were slowly cooled from the melt and not aged. Figure (4.5.1.3) shows plots of $\frac{dI(Q,T)}{dT}$ versus $T$ for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture, slowly cooling from the melt (cross) and slowly heating (filled square) after long time ageing. Apparently, no turning point is observed for unaged mixture. Similar result is obtained for the 4.3:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture slowly cooled from the melt (cross) and aged one day at room temperature. Thus, for $C_{30}/C_{36}$ pairs, in contrast to systems where the equilibrium is quickly attained, the mixed-demixed transition is determined only by slow heating of aged mixtures.
Plots of $dI(Q,T)/dT$ versus $T$ for several $C_{30}H_{62}/C_{36}D_{74}$ mixtures at a rate of 0.4°C are shown in figure[4.5.1.4]. Peak transition temperatures obtained in SANS heating curves are used to construct a temperature-composition diagram of $C_{30}H_{62}/C_{36}D_{74}$ mixtures, as illustrated in figure[4.5.1.5]. The temperature-composition diagram shows that the transition behavior is composition independent, which is consistent with the result for $C_{30}H_{62}/C_{36}H_{74}$ mixtures[1]. The line so determined in the phase diagram may be the binodal line which often has a parabolic shape in other binary systems. The SANS-based transition temperature obtained is about 45°C for the $C_{30}H_{62}/C_{36}D_{74}$ mixture.

According to Stehling et al[10] and Bates et al[18], the melting point of $C_{36}H_{74}$ is about 4°C greater than that of $C_{36}D_{74}$ due to the isotopic effect. A similar isotopic effect could be expected on the $C_{30}H_{62}/C_{36}D_{74}$ mixtures. For semi-crystalline polymers[16], the transition temperature decreases systematically with increasing cooling rate. Since our samples were treated by previous quenching before slow heating, the samples could contain vacancies despite long time ageing. Thus, on the grounds of an isotope effect and the presence of vacancies, the nearly six degree depression of the transition temperature of $C_{30}H_{62}/C_{36}D_{74}$ mixtures compared to that of $C_{30}H_{62}/C_{36}H_{74}$ mixtures measured by DSC may be justified. The $C_{30}H_{62}/C_{36}D_{74}$ data here suggest that the transition temperatures observed in neutron scattering corresponds to those reported by Dorset[1] at about 51°C for $C_{30}H_{62}/C_{36}H_{74}$.
Figure 4.5.1.4) Plots of $dI(Q,T)/dT$ as a function of temperature for several C$_{30}$H$_{62}$/C$_{36}$D$_{74}$ mixtures quenched from the melt to room temperature, aged for a long time, and then slowly heated to higher temperatures at a rate of $0.4^\circ$C/min. The mixtures are (a) 4:1, (b) 1:1, (c) 3:8, (d) 1:4, and (e) 1:9.
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Figure (4.5.1.5) The partial phase diagram of C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}D\textsubscript{74} mixtures, the line is the boundary between solid solution and fractionated solid.

Figure (4.5.1.6) Plot of dI(Q,T)/dT as a function of temperature for the 1:1 C\textsubscript{30}D\textsubscript{62}/C\textsubscript{36}H\textsubscript{74} mixture quenched from melt to room temperature, aged for a long time, and then slowly heated to the melt at a rate of 0.4°C/min.

As seen in the previous section, the scattering patterns of the 1:1 C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}D\textsubscript{74} are quite different from those of the 1:1 C\textsubscript{30}D\textsubscript{62}/C\textsubscript{36}H\textsubscript{74}. Whether the isotopic effect also influences the transition temperature, at least for C\textsubscript{30}/C\textsubscript{36} pairs, should be examined. Figure (4.5.1.6) shows a plot of dI(Q,T)/dT versus T for the 1:1 C\textsubscript{30}D\textsubscript{62}/C\textsubscript{36}H\textsubscript{74} mixture. It is found that the transition temperature is the same as that of the 1:1 C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}D\textsubscript{74}, i.e., no isotopic effect on the transition temperature is found within the experimental errors. We have ruled out possibilities that there are impurities and large differences in the experimental conditions.
The question raised is why should the demixing process be influenced by the isotopic effect but not the transition temperature? The different behavior of the demixing process in $C_{30}H_{62}/C_{36}D_{74}$ and $C_{30}D_{62}/C_{36}H_{74}$ mixtures can be explained as a direct consequence of the differences in melting points and volumes between protonated and deuterated species[10,18] and perhaps the interaction between protonated and deuterated species[19]. The demixing rate depends on the composition and is influenced by the isotope effect, which will be quantitatively discussed later. The transition temperature here, however, is determined by a critical dissolution of domains (or clusters). Since the dissolution of clusters in mixtures should involve the diffusion of molecules along the longitudinal direction, the migration of the molecules needs space. Vacancies in samples would be the only source of transient paths for the chain migration. At lower temperatures, vacancies in an aged sample which has undertaken an ordering process would not be numerous or large enough for both $C_{30}H_{62}/C_{36}D_{74}$ and $C_{30}D_{62}/C_{36}H_{74}$. In this case, the movement of paraffin molecules along their chain orientations becomes impossible because there is no chance or enough space for molecules to take their first step forward. As the temperature increases, the chains become more disordered and the concentration of partial vacancies increases. The paraffin molecules would start to migrate. That paraffin molecules migrate across lamellar boundaries from one layer to another would cause lamellae to collapse and chains to get intermixed. In this process, the dissolution of domains would be dependent on the concentration of partial vacancies.

The experimental results have indicated that the dissolution of domains almost is an instantaneous action. It is suggested that there should be little hindrance for continuing motion of another paraffin molecule after an original vacancy is bridged. We have noted the volume difference between $C_{30}H_{62}/C_{36}D_{74}$ and $C_{30}D_{62}/C_{36}H_{74}$ due to the isotope effect[18]. But, the present data seem to indicate that this difference is not significant enough to influence motion of chain molecules in an aged sample.

Figure(4.5.1.7) shows plots of the integrated intensity or invariant $Q_1(=\int Q^2)$ (left hand side) and $dQ/dT$ (right hand side) versus temperature $T$ for several $C_{30}H_{62}/C_{36}D_{74}$ mixtures. The curve shapes of $Q_1$ versus $T$ and $dQ/dT$ versus $T$ plots are very similar to those of $I$ versus $T$ and $dI/dT$ versus $T$. The transition temperatures determined are also
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Figure 4.5.1.7  Plots of $Q_1$ and $dQ_1/dT$ versus $T$ for several $C_{36}H_{62}/C_{36}D_{74}$ mixtures: (a) 4.3:1, (b) 1:1, (c) 3:8, (d) 1:4, and (e) 1:9.
close to 45°C within the uncertainty of the experiments. Since the invariant is not corrected for the interfacial region, the results would indicate that increased mixing occurs initially at interfacial regions and then lamellae. Detailed information about the interfacial region remains to be investigated. It is noted that the invariant do not diminish toward zero at high-temperature. Actually, even without a demixing, there still exist local heterogeneities due to conformational disorders which may contribute to the scattered intensity. The invariant may therefore be overestimated.

Figure(4.5.1.8) show the plot of the invariant as a function of time for the 1:4 C$_{30}$H$_{62}$/C$_{36}$D$_{74}$ mixture quickly heated rather than slowly heated to chosen temperatures. These data also indicate a delay phenomena in the dissolution of clusters.

4.5.2 LONG SPACING

Long spacings of C$_{30}$H$_{62}$/C$_{36}$D$_{74}$ mixtures are determined by application of Bragg’s law to peaks in the corrected scattering patterns. Some results are summarized in table 4.5.2.1. Ageing times are about six months and one year. The long spacings are found to be very different from those of the pure components. We take the 1:1 and 1:4 mixtures as examples for following discussion.
TABLE 4.5.2.1 comparisons of the long spacing

<table>
<thead>
<tr>
<th>C30/C36</th>
<th>4.3/1</th>
<th>1/1</th>
<th>3/8</th>
<th>1/4</th>
<th>1/9</th>
</tr>
</thead>
<tbody>
<tr>
<td>short time</td>
<td>87(570 min)</td>
<td>78(750 min)</td>
<td>180(600 min)</td>
<td>205(330 min)</td>
<td></td>
</tr>
<tr>
<td>L(Å)</td>
<td>175</td>
<td>94</td>
<td>90</td>
<td>205</td>
<td>235</td>
</tr>
</tbody>
</table>

The long spacing of the 1:1 C<sub>30</sub>H<sub>62</sub>/C<sub>36</sub>D<sub>74</sub> in 570 minutes after quenching is 87Å. After long time ageing, the equilibrium long spacing of the mixture is 94Å. Both values are very close to the sum of long spacings of the two pure components, 89Å[1], within the uncertainty of the experiments. Therefore, along the longitudinal direction, almost sequence of separated C<sub>30</sub>H<sub>62</sub> and C<sub>36</sub>D<sub>74</sub> lamellae should be arranged in an alternative way. If the sequence of separated lamellae were totally random, the long spacing of the mixture would be somewhere between C<sub>30</sub>H<sub>62</sub> and C<sub>36</sub>D<sub>74</sub> long spacings. However, we can not totally rule out possibility that separated lamellae are randomly arranged along longitudinal direction of chains in few layers because the long spacing at Q=0.136Å<sup>-1</sup> is detectable and shorter than that of pure C<sub>36</sub>D<sub>74</sub>. It is also possible that C<sub>30</sub>H<sub>62</sub> chains dilute in C<sub>36</sub>D<sub>74</sub> lamellae and the reverse, at least within the time scale of experiments. In a layer, separated C<sub>30</sub>H<sub>62</sub> and C<sub>36</sub>D<sub>74</sub> lamellae are considered to interact to some extent by intrusion into the neighboring lamellae. The edges of lamellae do not keep in good order and boundaries between lamellae are complicated. These may be the reasons why the measured long spacings are not exactly equal to the sum of long spacings of the two pure components.

For the 1:4 C<sub>30</sub>H<sub>62</sub>/C<sub>36</sub>D<sub>74</sub> mixture, the equilibrium morphology after quick quenching is assumed to be islands of the minority component C<sub>30</sub>H<sub>62</sub> isolated in the sea of the majority component C<sub>36</sub>D<sub>74</sub>, as schematically shown in figure(4.5.2.1). The lamellae of the minority component stack in an orientationally correlated fashion and build up lamellar domains. The orientations of these lamellar domains, however, are randomly distributed. The extreme case is that the number of chains in domains of the minority component approaches one, which indicates a homogeneous mixture.

Several possible lamellar arrangements are hypothetically spelled out for discussion. Figure(4.5.2.2) represents different possibilities for the 1:4 mixture at equilibrium state...
although other structures may be conceived. Since lamellar arrangements are one dimensional view, the domain shapes are difficult to draw. The white and black rectangle in the figure represent \( C_{30}H_{62} \) and \( C_{36}D_{74} \) chains and their ratio is 1:4. For case a, \( C_{30}H_{62} \) and \( C_{36}D_{74} \) lamellae are strictly arranged in terms of the molar ratio. The lateral dimension of the \( C_{30}H_{62} \) lamellae is the same as that of \( C_{36}D_{74} \), i.e., the size of \( C_{30}H_{62} \) clusters is equal to that of \( C_{36}D_{74} \). There is no correlation between lamellae in the longitudinal direction. For case b, only difference is that the chain length ‘averaging’ is accomplished by the interleaving of chains at the lamellar surface. Thus, there is a correlation between lamellae in the longitudinal direction. The cases c and d are different from a and b. The

![Figure](image)

**Figure (4.5.2.1)** The equilibrium distribution of \( C_{30}H_{62} \) clusters in a \( C_{36}D_{74} \) matrix for nonequimolar mixtures after quenching.

![Figure](image)

**Figure (4.5.2.2)** Possible lamellar arrangements for the 1:4 \( C_{30}H_{62} / C_{36}D_{74} \) mixture at equilibrium state. Black and white rectangles represent \( C_{36}D_{74} \) and \( C_{30}H_{62} \) chains, respectively.
average lateral dimension or average cluster size of the shorter chain lamellae in both cases are smaller than that of the longer chain lamellae. The smaller is the average cluster size of the minority component, the more is the cluster number, and therefore the shorter is the long spacing of the mixture. The case d shows some minority component in lamellae of the majority component and the reverse. The distances between two vertical lines in the figure indicate the average long spacings.

The measured long spacings are found not to be consistent with the average long spacing calculated from molar ratios. If it is assumed that the average number of chains in domains (or clusters) of the minority component are the same as those of the majority component, the calculated long spacing is 235Å which is longer than the measured value of 205Å. Clearly, the same lateral dimension of the two pure components is not acceptable. The case a is therefore immediately ruled out. The equilibrium long spacings we observe are so short that the case b would also be impossible. Our results suggest that the most probable structure in the 1:4 C$_{30}$H$_{62}$/C$_{36}$D$_{74}$ mixture is case d. Within the time scale of the experiments, especially in the early time of demixing, the separated lamellae would coexist with comixed lamellae. The structure may approach the case c after a very long time. The existence of a correlation between lamellae in the longitudinal direction due to the interleaving of chains at the lamellar surface, as shown in the case b, should be taken into account cases c and d. What is more, the conformational disorder and its effect on boundaries between lamellae should also be considered for an actual situation. Similar discussion would be available to other mixtures significantly unbalanced in concentration.

On the basis of the above discussions, the parameters, including the average length of the majority component part and effective length of the minority component in a period; and the average thickness of boundaries between lamellae, could be calculated by relevant models.

Very recently, Snyder et al[5] have found that the average domain size of C$_{30}$H$_{62}$ component in the 1:4 C$_{30}$H$_{62}$/C$_{36}$D$_{74}$ mixture is smaller than that in the case of the 1:1 mixture. Even for the 1:1 C$_{30}$H$_{62}$/C$_{36}$D$_{74}$ mixture, the average domain size of the two pure components are also found to be different[5]. The average domain size of the longer chain is found to be larger than that of the shorter chains. Their results imply that the domain shapes of the 1:1 mixture are not alike for the two pure components.
Figure (4.5.2.3) shows the long spacing as a function of annealing temperature for the 1:4 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture quickly quenched from the melt to chosen temperatures. The long spacings are obtained at the maximum time scale of the experiments. It can be seen that the 1:4 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture displays a conventional increase in the long spacing with increasing annealing temperature, consistent with the behavior of all oriented and unoriented systems. Our measurements on the temperature dependence of long spacing imply that the average size (lateral dimension) and therefore the number of \( \text{C}_{30}\text{H}_{62} \) clusters are dependent on the annealing temperature. Such a situation is schematically shown in figure (4.5.2.4). The average cluster size of \( \text{C}_{30}\text{H}_{62} \) is considered to increase but its number to decrease with increasing annealing temperature. The results here, along with temperature dependence of scattering patterns, indicate that mobile vacancies (activated vacancies), may play an important role in the demixing of the present system.

When the sample is quenched to higher temperatures, there are more mobile vacancies by which the molecular chains can migrate. When the sample is quenched to lower temperatures, it would have fewer mobile vacancies and the chains would not migrate as easily.
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Figure (4.5.2.5) The long spacing as a function of annealing time for the 1:1 \( C_{30}H_{62}/C_{36}D_{74} \) mixture quenched from the melt to 27°C.

Figure (4.5.2.6) The long spacing as a function of annealing time for the 3:8 \( C_{30}H_{62}/C_{36}D_{74} \) mixture quenched from the melt to 27°C.

Figure (4.5.2.7) A sketch of the change in long spacing with annealing time for the 1:1 \( C_{30}H_{62}/C_{36}D_{74} \) mixture (a) random mixture, (b) fractionated solid in shorter times, and (c) fractionated solid in longer times. Black and white rectangles represent \( C_{36}D_{74} \) and \( C_{30}H_{62} \) chains, respectively.

At very low temperatures, some of vacancies are frozen (immobile vacancies) and some molecules of minority component are therefore trapped in the matrix of majority component.

Figures (4.5.2.5) and (4.5.2.6) show the variation of long spacing with the annealing time for 1:1 and 3:8 \( C_{30}H_{62}/C_{36}D_{74} \). The long spacing is found to approach a constant within the time scale of the experiments, which indicates that initial arrangement of the structure can quickly reach an equilibrium although the growth of better fractionated solid should
take a very long time. Our measurements on the ageing time dependence of scattered intensity have indicated this. As an example, figure (4.5.2.7) schematically shows the change in the long spacing with the microphase separation for the 1:1 mixture. The distance between vertical lines indicates the average long spacing. The variation of boundaries between lamellae with annealing time is noteworthy. When initial arrangement of the structure is reached, the fractionation as totally separated domains becomes controlled both by the diffusion of molecules and by an ordering of individual lamella.

![Figure 4.5.2.7](image1)

Figure (4.5.2.8) shows representative plots of the long spacing as a function of temperature. These data represent the change in the long spacing during the dissolution of clusters. For the 1:4 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture, the long spacing remains a constant up to about 40°C. Above this temperature, the long spacing increases through a ‘transition region’ towards break point shown by an arrow. Similar curve shape is observed for the 1:9 mixture. Such a region where the long spacing rises steeply when the temperature approaches the melting point was also found in the crystallization of polyethylene [20-21]. For the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture, however, no such transition region is observed.

![Figure 4.5.2.8](image2)
4.5.3 ISOTOPE EFFECTS IN C30/C36 PAIRS

For C30/C36 pairs, the primary ‘driving force’ for the demixing process is the chain length mismatch [2, 9]. However, experimental data show that there is an additional effect due to the deuterium. The isotope effect in small organic molecules is not a new subject. It has been found [22] that if the hydrogen is substituted by deuterium in hydrocarbon liquids, the principal isotope effect is the small reduction in the molar volume. Bartell and Roskos [22] have demonstrated that this reduction in molar volume is primarily a consequence of the C-D bonds being slightly shorter than the corresponding C-H bonds. The isotope effect in binary polymer mixtures, as far as we know, was first predicted by Buckingham and Hentchel [23] on the basis of a thermodynamic analysis. Experimentally, the isotope effect in binary polymers with identical chemical structure was investigated by Bates et al [24] and Lapp et al [25]. Beginning with initial reports concerning liquid mixtures of protonated and perdeuterated polybutadiene, Bates et al have extended their work to polystyrene [26], polyvinylethylene and polyethylethylene [27]. They have demonstrated that the isotopic effect is a universal feature in these mixtures.

For present system, the isotope effect can lead to differences in melting points and volumes between pure components. For C30/C36 pairs, the differences in melting points are 6.4°C for the 1:1 C30H62/C36D74; 10.4°C for the 1:1 C30H62/C36H74; and 14.7°C for the 1:1 C30D62/C36H74. The ratio of chain volume \( V_\text{H} / V_\text{D} \) is 1.0052 [18]. As a consequence of these differences, crystallization rates of two components and therefore the demixing rate of mixtures as well as the arrangement of lamellar structure will change. We here suggest that if these differences become larger, as seen in the 1:1 C30D62/C36H74, the demixing may become a significant two-stage process within the time scale of the experiments.

Figure (4.5.3.1) schematically shows lamellar arrangements and structural changes for C30/C36 pairs. Since differences in melting points and chain volumes between two components in the 1:1 C30D62/C36H74 are greater, C36H74, accompanied by few C30D62, crystallizes much faster than pure C30D62. Consequently, enriched C36H74 lamellae would form before the separation of C36H74 and C30D62 from a cocrystallized state. Enriched C36H74 lamellae would tend to stack above one another along normal direction of lamellae and form a structure that may resemble the pure C36H74. The cocrystallized state of
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C_{30}H_{62}/C_{36}D_{74} melt → quenched

very few C_{36}D_{74} domains + coexistence of two components

shorter times → equilibrium state

alternation

heated

coaexistence of two components

Figure(4.5.3.1) A sketch for lamellar arrangements and structural changes of 1:1 C_{30}/C_{36} pairs. Black and white rectangles here represent C_{36}H_{74} and C_{30}D_{62} lamellae, respectively.
C₃₆H₇₄ and C₃₀D₆₂ components becomes significantly unbalanced in concentration due to the first stage of the demixing. In this case, the separation of C₃₆H₇₄ and C₃₀D₆₂ from the cocrystallized state, the second stage of the demixing, and the morphology may be very similar to that in the 1:4 C₃₀H₆₂/C₃₆D₇₄. Within the time scale of the experiments, the smaller C₃₆H₇₄ clusters would be isolated in the matrix of C₃₀D₆₂. After long time ageing, the structure of the 1:1 C₃₀D₆₂/C₃₆H₇₄ reaches an equilibrium state where separated C₃₀D₆₂ and C₃₆H₇₄ lamellae are alternatively arranged in longitudinal direction of chains but there are larger domains of C₃₆H₇₄ in normal direction. When aged 1:1 C₃₀D₆₂/C₃₆H₇₄ is heated up to certain extent, the C₃₀D₆₂ and C₃₆H₇₄ lamellae in layers with alternative arrangement become mixed. However, C₃₆H₇₄ stacks may not mixed with C₃₀D₆₂ because they are larger and more compact[5]. When the temperature is further raised, the C₃₀D₆₂ component becomes dissolution. This can induce the dissolution of C₃₆H₇₄ which coexists with C₃₀D₆₂. The C₃₆H₇₄ stacks disappear when the temperature is higher than C₃₆H₇₄ melting point.

For the 1:1 C₃₀H₆₂/C₃₆D₇₄, the morphology at very short time after quenching is totally disordered. The coexistence of C₃₀H₆₂ and C₃₆D₇₄ chains rapidly develops into a alternative arrangement of separated lamellae within the time scale of the experiments. The Only difference in equilibrium structure of the 1:1 C₃₀H₆₂/C₃₆D₇₄ is that separated C₃₀D₆₂ and C₃₆H₇₄ lamellae are also alternative along normal direction.

Our SANS data of 1:1 C₃₀/C₃₆ pairs strongly support above structural arrangements and changes. The more pronounced intensity at Q=0.135Å⁻¹ and the weaker intensity at Q=0.082Å⁻¹ in the scattering patterns of the 1:1 C₃₀D₆₂/C₃₆H₇₄ are evidences. We note that the scattering pattern of the 1:1 C₃₀D₆₂/C₃₆H₇₄ at Q=0.082Å⁻¹ is similar to that of the 1:4 C₃₆H₇₄/C₃₀D₆₂ mixture. The temperature dependence of the scattered intensity also clearly shows structural changes. The two-stage process in lamellar dissolution of the 1:1 C₃₀D₆₂/C₃₆H₇₄ is observed. It can be expected that the order of two-stage demixing increases in going from C₃₆H₆₂/C₃₀D₇₄ to C₃₀H₆₂/C₃₆H₇₄ to C₃₀D₆₂/C₃₆H₇₄.

Although there is a stronger peak at Q=0.08Å⁻¹ related to the microphase separation in the scattering pattern of the 1:1 C₃₀H₆₂/C₃₆D₇₄, as seen in figure(4.4.5.1), we can not say that the demixing rate in the 1:1 C₃₀H₆₂/C₃₆D₇₄ must be faster than the 1:1 C₃₀D₆₂/C₃₆H₇₄.
Actually, weak or strong of scattering peaks at \( Q=0.08\,\text{Å}^{-1} \) does not indicate the demixing rate. Snyder et al [5] have recently found that for \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixtures, the time required for the 1:4 mixture to reach an equilibrium is shorter than that for the 1:1 mixture. SANS intensity of the 1:4 mixture at \( Q=0.08\,\text{Å}^{-1} \), however, is much weaker than that of the 1:1 mixture, as seen in section 4.4. It has been previously explained as smaller sizes of the \( \text{C}_{30}\text{H}_{62} \) clusters in the 1:4 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) than those in the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \). Similarly, the average size of \( \text{C}_{36}\text{D}_{74} \) clusters separated from the coexistence state in the 1:1 \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) is expected to be smaller because the coexistence state is unbalanced in concentration although the average size of domains for the 1:1 \( \text{C}_{36}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) may be larger than those of 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture due to larger domains \( \text{C}_{36}\text{D}_{74} \). This would be the reason why there is the weaker peak at \( Q=0.08\,\text{Å}^{-1} \) in the scattering patterns of the 1:1 \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) within the time scale of the experiments.

The difference in the scattered intensity at the lowest accessible \( Q \) may be also attributed to the isotopic effect. Since the isotope effect can cause a small reduction in the molar volume[18], the chain volume of \( \text{C}_{36}\text{D}_{74} \) should be slightly smaller than \( \text{C}_{36}\text{H}_{74} \). Thus, the vacancy volume should be slightly smaller in the \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) than that in the \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{H}_{74} \) due to a decrease in the difference of chain volume. On the other hand, the isotope effect results in a larger vacancy volume in the \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) than that in the \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{H}_{74} \) due to an increase in the difference of chain volume. Consequently, the vacancy volume in the 1:1 \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) is larger than that in the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \). This may cause somewhat stronger scattered intensity at the lowest accessible \( Q \) in the 1:1 \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \).

The demixing rate and the isotope effect on demixing rate will be quantitatively discussed in Chapter 5.

### 4.5.4 ONE DIMENSIONAL MODEL

We consider a separated domain structure. The lamellae stack in an orientation correlated fashion and build up a lamellar structure. The SANS intensity of this model can be related to the one-dimension correlation function \( \gamma_1(r) \), which describes the spatial correlations.
of the scattering length density fluctuations and is defined as the average

\[ \gamma_1(r) = \langle [b(r_0) - \langle b \rangle][b(r_0 + r) - \langle b \rangle] \rangle \]  

(4.5.4.1)

where \( b(r) \) denotes the scattering length density distribution along a trajectory normal to the lamellae, \( \langle b \rangle \) is the mean scattering length density and the angle brackets indicate averaging over all points \( r_0 \). The scattering length density correlation function \( \gamma'(r) \) can be normalized as

\[ \gamma(r) = \gamma_1(r) / \langle b^2 \rangle \]  

(4.5.4.2)

where \( \langle b^2 \rangle \) is the average scattering length density fluctuation. The fully background corrected intensity is related to \( \gamma(r) \) as shown in equations (4.5.4.3) and (4.5.4.4)

\[ \gamma_1(r) = \int_0^\infty 4\pi I(Q)Q^2 \cos(Qr)dQ \]  

(4.5.4.3)

or

\[ \gamma(r) = \frac{\int_0^\infty I(Q)Q^2 \cos(Qr)dQ}{\int_0^\infty I(Q)Q^2dQ} \]  

(4.5.4.4)

Note that the correlation function contains \( IQ^2 \), and so the correlation function is the Fourier inversion of the scattered intensity plotted in a way of \( IQ^2 \) as a function of wavevector \( Q \). The function represents the probability of finding physical mass or scattering length density as a function of distance \( r \) within the material from an origin.

The correlation function is calculated by the VAX computer with a Fortran program. An example of a computed correlation function is shown in figure (4.5.4.1) for the 3:8 \( C_{30}H_{62}/C_{36}D_{74} \) mixture aged for a long time at room temperature and measured at 26°C, indicating how parameters can be extracted. The parameters obtained from figure (4.5.4.1) are schematically indicated in figure (4.5.4.2)

From figures (4.5.4.3) to (4.5.4.5), representative correlation functions are shown for aged \( C_{30}H_{62}/C_{36}D_{74} \) mixtures. As seen from these figures, the first peaks related to the long spacings of the lamellar structure, become difficult to locate as the temperature is raised up to about 46°C, independent of the composition. The results are in agreement with the
45°C transition temperature determined. The average length of the major component part and effective length of the minor component in a period are obtained from the correlation function. Plots of these parameters as a function of temperature are shown in figure(4.5.4.6). These parameters show the same behaviour as that of the long spacing. It should be pointed out that if there is the existence of the interfacial region between separated domains, its thickness has been incorporated into the average length of the majority component part. The long spacings obtained from the correlation function at room temperature are summarized in table 4.5.4.1. These results are in agreement with those determined from the Bragg law.

Figure(4.5.4.1) Representative normalized correlation function plot for the 3:8 C₃₀H₆₂/C₃₆D₇₄ mixture showing how information can be extracted from data: mn is an extrapolation of linear portion of the \( \gamma(r) \) function. mn crosses the \( \gamma(r)=0 \) axis at a point giving the value of the expression \( L_m(1-V_m) \). In our study, \( V_m \) is the overall volume fraction of one phase and \( L_m \) is effect length of the minority component. The extrapolation of mn to \( r=0 \) gives the value of the invariant, \( Q_1 \), for unnormalized data. op is drawn tangent to the minimum of the \( \gamma(r) \) function and intersects mn at point w. The \( r \) value of point w gives \( L_m \). L, the average value for the long spacing, is given by the first maximum of the \( \gamma(r) \) function.

Figure(4.5.4.2) Indications of the long spacing of a mixture, L, the effective length of the lamellae of the minority component, \( L_m \), and the average length of the part of the majority component, \( L-L_m \), obtained from the correlation function.
Figure (4.5.4.3) The correlation function $\gamma(r)$ for aged 4.3:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture at (a) 27°C and (b) 46°C.

Figure (4.5.4.4) The correlation function $\gamma(r)$ for aged 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture at (a) 27°C and (b) 47°C.

Figure (4.5.4.5) The correlation function $\gamma(r)$ for aged 3:8 $C_{30}H_{62}/C_{36}D_{74}$ mixture at (a) 24°C and (b) 46°C.
Table 4.5.4.1 values of the long spacing at room temperature

<table>
<thead>
<tr>
<th>L(Å)</th>
<th>C30/C36</th>
<th>4.3/1</th>
<th>1/1</th>
<th>3/8</th>
<th>1/4</th>
<th>1/9</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>94</td>
<td>86</td>
<td>195</td>
<td>290</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.5.4.6 Parameters obtained from the correlation function as a function of temperature for (a) 4.3:1, (b) 1:1, and (c) 3:8. The open and filled triangle are the average length of the major component part and effective length of the minority component in a period.

The effective length of C_{30}H_{62} is found to be about 32 Å for 1:1 and 3:8 mixtures. The average volume fractions of the effect lengths of C_{30}H_{62} obtained are about 30% for 1:1, 28% for 3:8. For the 1:1 mixture, which is assumed to be an random sequence of pure components, the average length of C_{36}D_{74} part is 62 Å. Since the long spacing of pure C_{36}D_{74} is about 47.5 Å[29], the thickness of the interfacial region is estimated to be about...
15Å between lamellae. For the 4.3:1 mixture, the effective length of C\textsubscript{36}D\textsubscript{74} lamellae and the average length of C\textsubscript{36}H\textsubscript{62} part in a period are calculated to be 36Å and 139Å. The results indicate that the average sequence of the 4.3:1 C\textsubscript{36}H\textsubscript{62}/C\textsubscript{36}D\textsubscript{74} structure would be one pure C\textsubscript{36}D\textsubscript{74} lamellae and three pure C\textsubscript{36}H\textsubscript{62} lamellae in a period. The average thickness of the interfacial region between lamellae is estimated to be about 17Å.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.5.4.7.png}
\caption{The correlation function $\gamma(r)$ for (a) 1:4 and (b) 1:9 at 27°C.}
\end{figure}

It is noted that the maxima in plots of the correlation function for 1:4 and 1:9 mixtures, as shown in figure(4.5.4.7), are very indistinct at room temperature. The long spacings estimated from arrow positions are about 195Å for the 1:4 mixture and about 290Å for the 1:9 mixture. The effective length of the C\textsubscript{36}H\textsubscript{62} lamellae is 35Å for both mixtures. The average sequences of separated lamellae in a period can be determined: one C\textsubscript{36}H\textsubscript{62} lamella and three C\textsubscript{36}D\textsubscript{74} lamellae for the 1:4 mixture; one C\textsubscript{36}H\textsubscript{62} lamella and five C\textsubscript{36}D\textsubscript{74} lamellae for the 1:9 mixture. Comparing the sequence ratio with corresponding molar ratio, it is found that the average cluster size of the C\textsubscript{36}H\textsubscript{62} component in the 1:9 mixture is smaller than that in the 1:4 mixture. The average thickness of the interfacial region is estimated to be about 17Å for the two mixtures. The results also rule out possibilities that the second peaks of scattering patterns are long spacings. We note that under these experimental conditions, the structure could not be a typical two phases and parameters obtained could larger errors.
4.5.5 A MODEL OF THE INTERFACIAL REGION

As known, it is difficult to get the information of the interfacial region between the two phases by the electron diffraction and differential scanning calorimetry mainly due to the limited or poor sensitivity. Small angle scattering technique, however, is at present probably the only method capable of giving information of the interfacial region. In this section, the interfacial region of C\textsubscript{30}H\textsubscript{62}/C\textsubscript{30}D\textsubscript{74} mixtures is investigated.

4.5.5.1 THEORETICAL BACKGROUND

The paraffin mixture here is supposed to have one dimensional density (scattering length density for SANS) fluctuation along a direction normal to lamellar interfaces\cite{30-32}. The assumed model of lamellar structure is shown in figure(4.5.5.1). The density variation \( \eta(z) \) along the z axis is periodic because of a periodic arrangement of lamellae. For an ideal two phase system, the density variation \( g(z) \) is discontinuous from one lamella to the next. If there exists interfacial region, the density variation \( \eta(z) \) generally deviates from the \( g(z) \) of the ideal two phase case where the density continuously changes from one lamella to the next. If \( h(z) \) is defined as a smoothing function related to the thickness of interfacial region, the density variation \( \eta(z) \) for a pseudo two phase system can be expressed by the one dimensional convolution products of function \( g(z) \) and \( h(z) \). Here, only scattering normal to boundaries is considered.

\[
\eta(z) = g(z) \ast h(z) = \int_{-\infty}^{\infty} g(u)h(z-u)\,du
\tag{4.5.5.1}
\]

The structure amplitude of the system, \( F(Q) \), is given by the Fourier transform of the function \( \eta(z) \)

\[
F(Q) = \mathcal{F}\{\eta(z)\}
\tag{4.5.5.2}
\]

\[
\mathcal{F}\{\eta(z)\} = \int_{-\infty}^{\infty} \eta(z)\exp(iQz)\,dz
\tag{4.5.5.3}
\]

Equation(4.5.5.3) can be rewritten as

\[
\mathcal{F}\{\eta(z)\} = \mathcal{F}\{g(z)\}\mathcal{F}\{h(z)\}
\tag{4.5.5.4}
\]

The scattered intensity \( I(Q) \) is therefore obtained by
The scattered intensity for any system can be expressed by

$$I(Q) \propto |F(Q)|^2 = I_g(Q)I_h(Q)$$  \hspace{1cm} (4.5.5.5)

where

$$I_g(Q) = |\Im\{g(z)\}|^2$$

$$I_h(Q) = |\Im\{h(z)\}|^2$$  \hspace{1cm} (4.5.5.5')

The scattered intensity for any system can be expressed by

$$I(Q) \propto \langle \eta^2 \rangle V \int \gamma(r) \exp[i(Q \cdot r)] dr$$  \hspace{1cm} (4.5.5.6)

where the mean square density fluctuation $\langle \eta^2 \rangle$ is given for an ideal two phase system by

$$\langle \eta^2 \rangle = (\rho_1 - \rho_2)^2 \phi_1 \phi_2$$  \hspace{1cm} (4.5.5.7)

where $\rho_i$ is density and $\phi_i$ volume fraction of $i$th phase. The function $\gamma(r)$ is the correlation function of density fluctuations. The variable $Q$ is a wavevector defined as usual. $V$ is

---

Figure (4.5.5.1) A model of lamellar structure. The disorder is not shown for clarity.
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irradiated volume. For SANS, \((\rho_1 - \rho_2)^2\) is replaced by scattering length difference \((b_D - b_H)^2\).

For an isotropic system, equation (4.5.6) is expressed as

\[
I(Q) \propto V(\rho_1 - \rho_2)^2 \int \gamma(r) (\sin Qr / Qr)^4 \pi r^2 dr
\]

(4.5.8)

For small \(r\), the correlation function \(\gamma(r)\) is given by Debye, Anderson, and Brumberger[33] as

\[
\gamma(r) = 1 - \left(S_{sp} / 4\phi_1\phi_2\right) r + \cdots
\]

(4.5.9)

where \(S_{sp}\) is the specific surface of a system which is defined as a ratio of total area of the interfaces \(S\) of two phase to the irradiated volume of specimen \(V\).

From equations (4.5.8) and (4.5.9), we have

\[
\lim_{Q \to \infty} I(Q) \propto (\rho_1 - \rho_2)^2 2\pi SQ^{-4}
\]

(4.5.10)

or

\[
I_g(Q) = C_1 Q^{-4}
\]

(4.5.11)

The equation (4.5.10) means that for an isotropic system, the scattered intensity from an ideal two phase system is given according to the familiar Porod’s law at larger \(Q\).

The observed scattered intensity is not that for the perfectly oriented system along the direction perpendicular to lamellar interfaces. Shibayama and Hashimoto[34] have derived that the observed scattered intensity from an unaxially oriented one dimensional assembly of lamellar domains and compared the observed scattering intensity with meridional scattered intensity parallel to the assembly axis. According to their conclusion, scattered intensity along \(z\) direction perpendicular to lamellar interfaces is simply proportional to the observed intensity multiplied by \(Q^2\), given by

\[
I_e(Q, \mu = 0) \propto I_{obs}(Q, \mu)Q^2
\]

(4.5.12)

irrespective of the sharpness of the orientation distribution except for the perfect orientation as a singular point. Their results suggested that for a perfectly oriented system, the interfacial region can be determined by using the same equation as that for a randomly oriented system no matter how small the orientational perturbation is from perfectness.
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The smoothing function \( h(z) \), on the other hand, can be chosen as a step function or Gaussian function, as given by

\[
h(z) = \begin{cases} 
\frac{1}{E} & 0 \leq z \leq E \\
0 & z > E 
\end{cases}
\] (4.5.5.13)

or

\[
h(z) = (2\pi \sigma^2)^{-1/2} \exp(-z^2 / 2\sigma^2)
\] (4.5.5.14)

where \( E \) is defined as boundary thickness and \( \sigma \) the standard deviation.

If the smoothing function \( h(z) \) is given by a step function, \( I_h(Q) \) is obtained from equation (4.5.5.5')

\[
I_h(Q) = \sin^2(QE/2)/(QE/2)^2
\] (4.5.5.15)

If the smoothing function \( h(z) \) is given by Gaussian function, \( I_h(Q) \) is obtained by

\[
I_h(Q) = \exp(-\sigma^2Q^2)
\] (4.5.5.16)

If the interfacial region is assumed to be narrow, equations (4.5.5.15) and (4.5.5.16) can be approximated by, respectively

\[
I_h(Q) = 1 - (QE/2)^2 / 3 + O[(QE/2)^4]
\] (4.5.5.17)

\[
I_h(Q) = 1 - (Q\sigma)^2 + O[(Q\sigma/2)^4]
\] (4.5.5.18)

The relationship between \( E \) and \( \sigma \) is therefore obtained by

\[
E = 2(3^{1/2})\sigma
\] (4.5.5.19)

Then, according to equation (4.5.5.5), the scattered intensity \( I(Q) \) is readily obtained, respectively

\[
I(Q) = (\text{const.})Q^{-4} \sin^2(QE/2)/(QE/2)^2
\]

\[
= (\text{const.})Q^{-4}[1 - (QE/2)^2 / 3 + O[(QE/2)^4]]
\] (4.5.5.20)

\[
I(Q) = (\text{const.})Q^{-4} \exp(-\sigma^2Q^2)
\]

\[
= (\text{const.})Q^{-4}[1 - \sigma^2Q^2 + O[(Q\sigma/2)^4]]
\] (4.5.5.21)

Equations (4.5.5.20) and (4.5.5.21) allow easily graphical evaluations of the parameter \( \sigma \) and \( E \).
Instead of equation (4.5.5.19), a more general definition of the interfacial region thickness is given:

\[ E = \left| \frac{1}{l} \frac{d\eta(z)}{dz} \right|_{\eta=\Delta\rho/2} \]  

(4.5.5.22)

where \( \Delta \rho \) is the density difference. The density variation can be expressed as

\[
\eta(z) = \pi^{1/2} \Delta \rho \sum_{i=-N/2}^{N/2} \left\{ \text{Erf} \left( \frac{z + a - L_i}{\sqrt{2\sigma}} \right) - \text{Erf} \left( \frac{z - a - L_i}{\sqrt{2\sigma}} \right) \right\}
\]

(4.5.5.23)

with

\[
\text{Erf}(x) = \int_{0}^{x} \exp(-t^{2}) dt \]

(4.5.5.24)

where \( a \) is half thickness of lamella, \( N \) the number of pairs of lamellae in an assembly, and \( L_i \) the average lamellar spacing. From equations (4.5.5.22) and (4.5.5.23), the thickness of interfacial region is obtained for small \( \sigma \),

\[ E = (\sqrt{2\pi})\sigma \]  

(4.5.5.25)

In present work, equation (4.5.5.25) is used to estimate the thickness of interfacial region between lamellae.

### 4.5.5.2 EXPERIMENTAL ANALYSIS

#### 4.5.5.2.1 AGED PURE C₃₆D₇₄

The pure C₃₆D₇₄ aged for a long time was slowly heated to higher temperatures. Representative plots of lnIQ⁴ versus Q² are shown in figure (4.5.5.2). No information on the interfacial region is detectable in terms of the above analysis. It is not surprising because there is no difference, if anything, negligible small, in the scattering length between pure C₃₆D₇₄ lamellae. However, it does not mean that no interfacial region exists in boundaries between lamellae for pure paraffin samples, especially, for samples in short times after quenching and at higher temperatures. The interfacial region of pure paraffin samples can be determined by the method given in Chapter 3. The heuristic conclusion drawn here is that the interfacial region is detected by SANS only when systems separate into two phases with enough scattering length difference, in another word, we can determine the extent of microphase separation by tracing the variation of interfacial region.
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4.5.5.2.2 INCOMPLETELY AGED C_{30}H_{62}/C_{36}D_{74} MIXTURES

Figure (4.5.5.2) is representative plots of lnQ^4 versus Q^2 for the 1:4 C_{30}H_{62}/C_{36}D_{74} mixture without aged after slow cooling from the melt. Also, no detectable interfacial region is found. Similar results are also obtained from the 1:9 C_{30}H_{62}/C_{36}D_{74} which was standing at room temperature only one day after slow cooling from the melt. The results clearly demonstrate that under these experimental circumstances there is no existence of separated lamellae. The C_{30}H_{62} and C_{36}D_{74} chains coexist in the same lamellae which could interleave in longitudinal direction. We note that the results are consistent with previous discussions.

Figure (4.5.5.3) is representative plots of lnQ^4 versus Q^2 for the 1:4 C_{30}H_{62}/C_{36}D_{74} mixture without aged after slow cooling from the melt.
4.5.5.2.3 AGED C_{30}H_{62}/C_{36}D_{74} MIXTURES

Figure (4.5.5.4) shows a plot of \( \ln Q^4 \) versus \( Q^2 \) for the 1:4 \( C_{30}H_{62}/C_{36}D_{74} \) which was aged for about six months. The negative slope in the figure indicates that the formation of an interfacial region. The slope obtained is about -38 and the thickness \( E \) of the interfacial region is thus estimated to be about 16\( \AA \) in terms of equation (4.5.5.25). This value would be an equilibrium one between separated lamellae at room temperature. Similar results are also obtained for other compositions. The composition independence of equilibrium thickness of the interfacial region is found with uncertainties of the experiments. It is noted that the results are very close to those estimated from one dimensional correlation function.

![Figure (4.5.5.4)](image)

**Figure (4.5.5.4)** The plot of \( \ln Q^4 \) versus \( Q^2 \) for the 1:4 \( C_{30}H_{62}/C_{36}D_{74} \) mixture rapidly quenched from the melt to room temperature, and aged for about six months.

4.5.5.2.4 VARIATION OF INTERFACIAL REGION IN MIXTURES WITH TEMPERATURE

Figures (4.5.5.5) and (4.5.5.6) show representative plots of \( \ln Q^4 \) versus \( Q^2 \) for aged 1:1 and 3:8 \( C_{30}H_{62}/C_{36}D_{74} \) mixtures at different temperatures. Similar results are found for other data. Figure (4.5.5.7) shows plots of the thickness as a function of temperature for \( C_{30}H_{62}/C_{36}D_{74} \). It can be seen that the curve shape is similar to that of the invariant \( Q_1 \) (or I) versus \( T \). When the temperature is lower than 45°C, the thickness shows a constant or a slight decrease. A composition independence of a sudden decrease in thickness is observed when the temperature is close to 45°C. The interfacial region disappears instantaneously when the temperature is higher than 45°C. The temperature-dependent
values of $\Delta b^2 S$ obtained from intercepts in plots of $\ln Q^4$ versus $Q^2$ are shown in figure (4.5.5.8). Essentially identical results are observed. These results provide more evidences for the occurrence of a lamellar mixing transition. When the identity of the interfacial region is lost, separated lamellae would collapse and paraffin molecules are randomly mixed along their chain axis. The results again demonstrate that the morphological transition instantaneously finishes and the hindrance for the migration of paraffin molecules crossing boundaries is very little as soon as the mixing occurs.

Figure (4.5.5.5) Representative plots of $\ln Q^4$ versus $Q^2$ for the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture at different temperatures.

Figure (4.5.5.6) Representative plots of $\ln Q^4$ versus $Q^2$ for the 3:8 $C_{30}H_{62}/C_{36}D_{74}$ mixture at different temperatures.
Figure (4.5.5.7) The average thickness of interfacial region as a function of temperature for $C_{30}H_{62}/C_{36}D_{74}$ mixtures: (a) 1:1, (b) 3:8, (c) 1:4, and (d) 1:9.

The interfacial region is also measured for aged 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture quickly heated to higher temperatures, as shown in figure (4.5.5.9). Upon heating, a decrease in the thickness of interfacial region is observed, as seen above. However, the decrease in the interfacial region with increasing temperature shows a delay phenomena.
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Figure (4.5.5.8) The value of $\Delta b^2S$ as a function of temperature for $C_{30}H_{62}/C_{36}D_{74}$ mixtures: (a) 1:1, (b) 3:8, (c) 1:4.

Figure (4.5.5.9) The plot of thickness as a function of time for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture at different temperatures. The arrow indicates the aged state.

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4.5.5.2.5 VARIATION OF INTERFACIAL REGION WITH TIME

The variation of the interfacial region with annealing time is investigated. Representative plots of \( \ln I Q^4 \) versus \( Q^2 \) for the 1:4 \( C_{30}H_{62}/C_{36}D_{74} \) mixture quenched from melt to chosen temperatures are shown in figure (4.5.5.10). Plots of the thickness of the interfacial region as a function of annealing time are displayed in figure (4.5.5.11) at different temperatures. The variation of \( \Delta b^2/S \) with annealing time is shown in figure (4.5.5.12). It is interesting to note that if the sample was quenched to the lower temperature, 26°C, the parameter \( \sigma \) is not detectable even in the maximum time scale of the experiments although an increase in the difference of scattering length is observed. The interfacial regions are observed, however, for the sample quenched to higher temperatures within the time scale of experiments. The appearance of an interfacial region and its thickness in a non equilibrated state are found to be annealing temperature dependence. For example, at a given time of 300 minutes, \( E \) values are about 12Å at 33°C and about 16Å at 41°C.

![Figure (4.5.5.10) Representative plots of \( \ln I Q^4 \) versus \( Q^2 \) for the 1:4 \( C_{30}H_{62}/C_{36}D_{74} \) mixture quenched from the melt to considered temperatures.](image-url)
Figure (4.5.5.11) The thickness of interfacial region as a function of annealing time for the 1:4 C_{30}H_{62}/C_{36}D_{74} mixture quenched from the melt to chosen temperatures.

Figure (4.5.5.12) The variation of Δb^2S as a function of annealing time for the 1:4 C_{30}H_{62}/C_{36}D_{74} mixture quenched from the melt to chosen temperatures.
The results indicate that the demixing rate would be faster at higher temperatures than at lower temperatures. More important is that at 26°C, C_{30}H_{62} and C_{36}D_{74} lamellae are not completely separated within the time scale of the experiments. The possible structure in this case may be constructed by the interleaving of chains in boundaries so that there is a close correlation in the longitudinal direction between the length of chains. We note that no detectable interfacial region here corresponds to a very broad peak in scattering patterns.

4.5.6 PARACRYSTALLINE MODEL

4.5.6.1 THEORETICAL BACKGROUND

The purpose of this section is to examine the applicability to paraffin lamellae of paracrystalline models which are often used to describe superstructures. In a review article, Wilke [35] has summarized and discussed most paracrystalline models. For the one dimensional case, important concept introduced is the interfacial region between lamellae. In most cases, the density profile in this sort of model is given by a trapezium shape and the thickness of the interfacial region is supposed to be constant. Paracrystalline models have been used to fit scattering patterns of polymers [36-41]. On the basis of thermodynamic arguments, Schmidt and Killian [42] proposed that the interfacial region is proportional to the lamellar size. We try here to fit scattering patterns for the 1:1 C_{30}H_{62}/C_{36}D_{74} mixture.

There are several theoretical one or quasi one dimensional paracrystalline models reported [43-46]. For present system, SANS scattering patterns are fitted by the modified stack model [46]

\[ I(Q) = [I_B(Q) + I_C(Q)]Z(Q) \]  

(4.5.6.1)

where \( I_B \) is the scattered intensity from the limiting size of lamellar stack producing some broadening of the whole scattering curve and \( I_C \) the zero-order scattering at very low Q. \( I_B \) and \( I_C \) can be expressed as

\[ I_B(Q) = \frac{(\Delta \rho)^2 N}{Q^2} \left[ \frac{1 - F_1^2}{1 - F_2^2} \right] \right] + \frac{1 - F_2^2}{1 - F_1^2} \right] \]  

(4.5.6.2)

and

\[ I_C(Q) = \frac{2(\Delta \rho)^2}{Q^2} \left\{ \frac{F_2 (1 - F_1)^2}{1 - (F_1 F_2)^N} \right\} \]  

(4.5.6.3)
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where \( \Delta \rho \) is the density difference between phases, \( F_1 \) and \( F_2 \) are the Fourier transforms of thickness distribution of different phases, \( N \) is the number of repeating unit in the paracrystal. Unlike the Vonk correlation function, \( N \) here is finite rather than infinite. The transition term \( Z(Q) \) introduced by Tsvankin\[46\] is

\[
Z(Q) = \frac{2\pi}{Q^2E} |1 - \exp(-QEi)|^2
\]  

(4.5.6.4)

where \( E \) is thickness of the interfacial region.

In practice, the above formulae are not suitable for calculations. In order to do convenient numerical work, the original formulae should be cast into algebraic forms before fitting\[47\]. For this reason, equation(4.5.6.1) is rewritten as

\[
I(Q) = \frac{2(\Delta \rho)^2}{Q^2} \left\{ \text{Re} \left[ \frac{N(1 - F_1)(1 - F_2)}{(1 - F_1 F_2)} \right] + \text{Re} \left[ \frac{F_2(1 - F_1)^2[1 - (F_1 F_2)^N]}{(1 - F_1 F_2)^2} \right] \right\} Z(Q)
\]

(4.5.6.5)

On the basis of the theory of the Fourier transforms, \( F_1 \) and \( F_2 \) can always be given as

\[
F_1 = A \exp(-i\psi)
\]

(4.5.6.6)

\[
F_2 = B \exp(-i\phi)
\]

(4.5.6.7)

and

\[
\omega = \psi + \phi
\]

(4.5.6.8)

The parameters \( A, B, \psi \) and \( \phi \) depend on what kind of distribution function of phase lengths is chosen. After substituting \( F_1 \) and \( F_2 \) into equation(4.5.6.5), an algebraic form is given

\[
I(Q) = \frac{2(\Delta \rho)^2 Z(Q)}{Q^2} \left( \frac{C}{F} + \frac{D + G}{F^2} \right)
\]

(4.5.6.9)

where

\[
F = 1 + A^2B^2 - 2AB\cos \omega
\]

(4.5.6.10)

\[
C = N\{1 - A^2B^2 - A(1 - B^2)\cos \phi - B(1 - A^2)\cos \psi\}
\]

(4.5.6.11)

\[
D = B\{(1 - A^2)(1 - A^2B^2)\sin \omega \sin \phi + [(1 + A^2B^2)\cos \omega - 2AB] \sin \omega \}
\]

(4.5.6.12)

\[
D = B\{(1 + A^2)(1 - A^2B^2)\sin \omega \sin \phi + [(1 + A^2B^2)\cos \omega - 2AB] \sin \omega \}
\]

(4.5.6.13)

\[
G = A^NB^{N+1}\sin N\omega \{(1 - A^2B^2)[(1 + A^2)\cos \phi - 2A]\sin \omega - (1 - A^2)(1 + A^2B^2)\cos \omega - 2AB] \sin \phi\}
\]

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When generating the theoretical scattering patterns, we have to consider a variety of possibilities by choosing different kinds of thickness distribution functions for the two phases. As is known, the shapes of scattering curves depend on the thickness distribution function chosen, either the same kind or different kinds of functions for the two phases. We also have to consider the fact that the asymmetric distribution functions can be positively or negatively skewed, which also gives different scattering shapes. In present work, the Reinhold-Fisher (RF) distribution function [48] is considered for the both phases.

\[ H(x) = \frac{x - \varepsilon}{(\gamma < Y >)^2} \exp \left[ -\frac{(x - \varepsilon)}{\gamma < Y >} \right] \]  

with

\[ \varepsilon = < Y > (1 - 2\gamma) \]  

where \( < Y > \) is a mean length and \( \gamma \) is a parameter controlling both the skew and dispersion of the distribution. The parameters \( A, B, \psi, \) and \( \phi \) are therefore determined by the Fourier transforms, respectively,

\[ A = \frac{1}{1 + (Q\gamma_1 < Y_1 >)^2} \]  

\[ \psi = (Q\varepsilon_1 + \cos^{-1} \left[ \frac{1 - (Q\gamma_1 < Y_1 >)^2}{1 + (Q\gamma_1 < Y_1 >)^2} \right]) \]  

\[ B = \frac{1}{1 + (Q\gamma_2 < Y_2 >)^2} \]  

\[ \phi = (Q\varepsilon_2 + \cos^{-1} \left[ \frac{1 - (Q\gamma_2 < Y_2 >)^2}{1 + (Q\gamma_2 < Y_2 >)^2} \right]) \]  

From equations (4.5.6.9) to (4.5.6.19), the theoretical scattering patterns can be calculated by computer.

4.5.6.2 MODEL FITTINGS

In figure (4.5.6.1), comparisons of the experimental and theoretical curves are shown for aged 1:1 \( C_{30}H_{62}/C_{36}D_{74} \) mixture at different temperatures. Figure (4.5.6.2) gives fits of the paracrystalline model to experimental data for the 1:1 \( C_{30}H_{62}/C_{36}D_{74} \) mixture at different
Figure (4.5.6.1) Fits of the paracrystalline model to 1:1 C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}D\textsubscript{74} mixture which had been quenched from the melt to room temperature, aged at room temperature for a long time, and then slowly heated to higher temperatures. (a) 27 °C, \( \gamma_1=0.38 \), \( \gamma_2=0.26 \), \( Y_1=34\,\text{Å} \), \( Y_2=64\,\text{Å} \), \( E=16\,\text{Å} \). (b) 32 °C, \( \gamma_1=0.395 \), \( \gamma_2=0.264 \), \( Y_1=34\,\text{Å} \), \( Y_2=64\,\text{Å} \), \( E=16\,\text{Å} \). (c) 34.5 °C, \( \gamma_1=0.395 \), \( \gamma_2=0.264 \), \( Y_1=34\,\text{Å} \), \( Y_2=64\,\text{Å} \), \( E=16\,\text{Å} \). (d) 37 °C, \( \gamma_1=0.39 \), \( \gamma_2=0.285 \), \( Y_1=34\,\text{Å} \), \( Y_2=64\,\text{Å} \), \( E=16\,\text{Å} \). (e) 42 °C, \( \gamma_1=0.39 \), \( \gamma_2=0.288 \), \( Y_1=34\,\text{Å} \), \( Y_2=64\,\text{Å} \), \( E=12\,\text{Å} \). and (f) 44.5 °C, \( \gamma_1=0.4 \), \( \gamma_2=0.315 \), \( Y_1=33\,\text{Å} \), \( Y_2=64\,\text{Å} \), \( E=0\,\text{Å} \). The cross and empty square represent experimental and fitting data, respectively.
Figure (4.5.6.2) Fits of the paracrystalline model to the 1:1 C_{30}H_{62}/C_{36}D_{74} mixture which was quickly quenched from the melt to 27°C. 

(a) 150 min, $Y_1 = 0.48$, $Y_2 = 0.33$, $Y_1 = 28\text{Å}$, $Y_2 = 62\text{Å}$, $E = 0\text{Å}$, (b) 210 min, $Y_1 = 0.48$, $Y_2 = 0.302$, $Y_1 = 29\text{Å}$, $Y_2 = 62\text{Å}$, $E = 6\text{Å}$, (c) 270 min, $Y_1 = 0.47$, $Y_2 = 0.30$, $Y_1 = 30\text{Å}$, $Y_2 = 63\text{Å}$, $E = 8\text{Å}$, (d) 330 min, $Y_1 = 0.47$, $Y_2 = 0.30$, $Y_1 = 31\text{Å}$, $Y_2 = 63\text{Å}$, $E = 10\text{Å}$, (e) 450 min, $Y_1 = 0.435$, $Y_2 = 0.30$, $Y_1 = 32\text{Å}$, $Y_2 = 64\text{Å}$, $E = 12\text{Å}$, and (f) 510 min, $Y_1 = 0.47$, $Y_2 = 0.30$, $Y_1 = 32\text{Å}$, $Y_2 = 64\text{Å}$, $E = 12\text{Å}$. The cross and filled square represent experimental and fitting data, respectively.
Figure (4.5.6.3) Fits of the paracrystalline model to the 1:1 \( C_{30}H_{62}/C_{36}D_{74} \) mixture which had been quenched from the melt to room temperature, aged at room temperature for a long time, and then quickly jumped to successive higher temperatures. (a) 27°C for a long time, \( \gamma_1 = 0.19 \), \( \gamma_2 = 0.29 \), \( Y_1 = 33\text{ Å} \), \( Y_2 = 65\text{ Å} \), \( E = 16\text{ Å} \), (b) 28°C for 15 min, \( \gamma_1 = 0.192 \), \( \gamma_2 = 0.295 \), \( Y_1 = 33\text{ Å} \), \( Y_2 = 65\text{ Å} \), \( E = 14\text{ Å} \), (c) 41°C for 15 min, \( \gamma_1 = 0.31 \), \( \gamma_2 = 0.295 \), \( Y_1 = 31\text{ Å} \), \( Y_2 = 64\text{ Å} \), \( E = 10\text{ Å} \), and (d) 41°C for 45 min, \( \gamma_1 = 0.395 \), \( \gamma_2 = 0.365 \), \( Y_1 = 27\text{ Å} \), \( Y_2 = 58\text{ Å} \), \( E = 0\text{ Å} \). The cross and empty squire represent experimental and fitting data, respectively.

times after quenching. Figure (4.5.6.3) shows fits of the paracrystalline model to aged 1:1 \( C_{30}H_{62}/C_{36}D_{74} \) mixture quickly switched to successive higher temperatures. It can be seen that experimental data are fitted very well. In calculations, the data of phase lengths and the long spacings determined previously are used. We note here that the fit is in effect a five parameter fit and so not necessarily unique.

4.5.7 SURFACE FRACTAL PROPERTIES OF A PARAFFIN

In last few years, both theoretical and experimental work has demonstrated the existence of fractal dimension in porous materials, aggregates, and ramified material[49,50].
However, recent experiments also show that pure polyethylene crystals with both folded chain and extended chain have surface fractal dimensions from 2.2 to 2.8, depending on crystallizing conditions[51]. In this section, the surface fractal dimension of pure \( \text{C}_{36}\text{D}_{74} \) is investigated.

Fractal theory and calculations of the scattering function for the fractal properties have been treated in detail and summarized in reviews by Meakin[49] and Martin et al[50], respectively. Conclusively, the scattering patterns from fractal objects have a power-law form, i.e., \( I(Q) \propto Q^{-\alpha} \). Mass fractals give rise to the power-law scattering like

\[
I \propto Q^{-\alpha} \propto Q^{-D_m}
\]

(4.5.7.1)

where \( D_m \) is a mass fractal dimension. If an object is uniform, the scattering also produces a power-law profile which depends on the structure surface,

\[
I \propto Q^{-\alpha} \propto Q^{D_f-2D}
\]

(4.5.7.2)

where \( D_f \) is surface fractal dimension and \( D \) is dimension of a material. For uniform objects with smooth, nonfractal surfaces, \( D_f=2 \), and equation(4.5.7.2) gives the familiar Porod’s law; i.e., \( I(Q) \propto Q^{-4} \). Scattering measurements can distinguish difference between the mass fractals (1<\( \alpha \)<3) and surface fractals (3<\( \alpha \)<4). Surface structures whose scattering deviates from Porod’s law may have a fractal structure and the surface fractal dimension \( D_f \) can be obtained by a plot of log\( I(Q) \) versus log\( Q \) in terms of the equation(4.5.7.2).

Figure(4.5.7.1) shows log-log plots of the neutron scattered intensity versus wavevector for pure \( \text{C}_{36}\text{D}_{74} \) at short time ageing and long time ageing at room temperature after quenching. The values of \( \alpha \) are determined to be 3.20 for short time and 3.35 for long time by the least-squares method. Figure(4.5.7.2) is the same plot for the sample at 46°C. The straight line gives a slope of 3.0. Then, the corresponding dimensions are obtained, 2.8 for short time, 2.65 for long time, and about 3.0 at 46°C. The results show that the surface dimension of pure \( \text{C}_{36}\text{D}_{74} \) is the fractal at room temperature. The fractal dimensions of 2.8 and 2.65 are comparable to that of the extended chain crystal of polyethylene[51]. The diffusion of chains along their axis would play an important role in the fractal dimension and its change.
Figure (4.5.7.1) Log-log plots of the scattered intensity versus wavevector for pure \( \text{C}_{36}\text{D}_{74} \) at (a) short time ageing and (b) long time ageing.

Figure (4.5.7.2) Log-log plot of the scattered intensity versus wavevector for pure \( \text{C}_{36}\text{D}_{74} \) which had been aged for a long time after quenching, and then was heated to 46°C.
4.6 CONCLUSIONS

The microphase separation and equilibrium structure have been investigated for C30/C36 mixtures by using small angle neutron scattering (SANS). The experiments were designed in two ways. First, the samples studied were prepared by quickly quenching the melt to room temperature, and changes in the degree of demixing and chain conformation were followed. The effects of quench temperature and concentration on the kinetics of microphase separation have been qualitatively reported. Second, the quenching crystalline solid solutions were aged at room temperature for a long time, and then the microphase-separated C30/C36 mixtures were slowly heated up to the melt. The structural data were analyzed in terms of a modified Porod model, a one dimensional model, a paracrystalline model, and a fractal model. The principal results are summarized as follows.

(1) SANS data indicate that compared with slow cooling, the microphase separation in C30/C36 mixtures occurred almost instantaneously when the samples were rapidly quenched from the melt. No microphase separation was detected for the mixture slowly cooled and not aged.

(2) The scattering patterns have shown that the microphase separation is very sensitive to the quench temperature and dependent on concentration. The scattered intensity decreases and main peak becomes narrower as temperature increases and concentration becomes more unbalanced. It is suggested that the vacancies and conformational disorder play an important role in microphase separation. The quantitative study of effects of quench temperature and concentration on the kinetics of microphase separation will be reported in next Chapter.

(3) The average domain size of minority components (lateral dimension) increases with the increase in quench temperature and concentration. For 1:1 mixture, the equilibrium structure is found to be an alternating arrangement of lamellae. For samples unbalanced in concentration, the average sequences of separated lamellae in a period, however, are not strictly arranged in terms of the molar ratios.
(4) The transition temperature from a fractionated solid to a solid solution is found to be about 45°C, which is independent of the concentration, quench rate, and isotopic effect. It was also found that the mixing has an almost abrupt increase as the temperature approaches transition temperature.

(5) The demixing in C30/C36 mixtures involves an ordering process in individual lamellae. The average size of domains and rate of separation reach equilibrium within the time scale of the experiments while the ordering process can last very a long time (several months, one year, and even longer). Similarly, the mixing and conformational disorder are interdependent when aged samples are slowly heated above the transition temperature. It is suggested that the conformational disorder is still undergoing when the mixing has been largely completed.

(6) In the maximum age time (near one year), the equilibrium structure is still not totally separated lamellae. There is a correlation between lamellae in the longitudinal direction. The interfacial region between lamellae in non equilibrated samples depends on the quench temperature, the time of phase separation, and concentration. But, the interfacial regions are approximately the same size, about 17Å, when the samples reach their equilibrium.

(7) Because the isotopic effect causes significant differences in melting points and volumes between pure components, the microphase separation in D/H pair becomes a two-step process, i.e., the precipitation of some pure H component precedes the separation of H and D components from the mixed state. This leads to differences in overall rate of demixing for the different pairs. More details will be reported in next Chapter.

(8) If the fractionated solids of C30/C36 mixture are assumed to be a superstructure (or superlattice-like structure), the paracrystalline model can be used to describe its structures. We here have successfully tested the applicability to paraffin mixture structure of the paracrystalline model.
(9) It was found that the scattered intensity of pure C$_{36}$D$_{74}$, which was quickly quenched from melt to room temperature, obeys a power law for wavevector over a wide Q range. The exponent is smaller than 4 given by Porod's law. If it is assumed that the boundary between lamellae has the fractal surface, the fractal dimension is 2.8 for the shorter time ageing and 2.65 for the longer time ageing. The higher dimension could indicate that the interfacial region is more disordered. After long time ageing, the interfacial region should become more ordered, and therefore its dimension decreases.
4.7 REFERENCES

5. R.G. Snyder, M.C. Goh, V.J.P. Srivatsavoy, and H.L.Strauss, J. Phys. Chem. 96, 10008 (1992), therein references
15. W. Wu and G. Wignall, Polymer 26, 661 (1985)
Chapter 4  Studies of Binary Paraffin Mixtures by SANS

34. M. Shibayama and T. Hashimoto, Macromolecules 19, 740 (1977)
42. H. Schmidt and H. Killian, 5th International Conference on Small Angle Scattering, 1980
43. D. Tsveankin, Vysokomol. Soyed. 6, 2078 (1964)
5.1 INTRODUCTION

The kinetics of the phase separations have been of great interest in the past decade [1]. The dynamical scaling and apparent universality in the late-stage kinetics have been a focus of this interest. Conservation laws are known to be the most important factor in governing the behaviour of late-stage kinetics. However, the influences of vacancies, grain boundaries, elastic distortions, and stoichiometry on the kinetics should be also taken into account although they are not as well understood. The kinetics in many systems, including binary alloys, binary fluids, polymers, glasses, ferroelectric crystals, and magnetic materials, have been extensively studied.

The study of kinetics of phase separation in paraffin mixtures is few [2]. The theories of phase separation have not been tested for this system yet. However, this system is important because the demixing occurs in a highly crystalline solid and involves conformational ordering. In this Chapter, the kinetics of paraffin mixtures is systematically investigated and results are related to current theories.

The primary results showing the demixing and dissolution have already been given in Chapter 4 and some elementary theoretical points have been discussed in Chapter 1.

The kinetics of demixing process for \( C_{30}H_{62}/C_{36}D_{74} \) mixtures can be displayed in several ways. We here discuss the demixing in terms of the invariant \( Q(t) \) and scattered intensity \( I(Q,t) \) near peak positions. The time evolution of the invariant will provide a broad overview of the demixing processes. The demixing and dissolution kinetics will also be described by models.
5.2 BASIS OF THE METHOD

By integrating the observed intensity $I(Q)$ over the entire wavevector $Q$, one can evaluate the integrated intensity or the invariant $Q_1$ defined by

$$Q_1 = 4\pi \int_0^\infty I Q^2 dQ$$

(5.1)

For SANS measurements, the invariant is equal to the mean-square deviation of the scattering length from the mean throughout a sample. If, instead of the observed scattered intensity, the correction for the ‘background’ has been made from a plot of $IQ^4$ versus $Q^4$, the resultant $Q_1$ represents only the contribution to the mean-square scattering length deviation in the sample and excludes the contribution from local heterogeneities due to thermal and concentration fluctuations. For a two phase system with sharp phase boundaries, $Q_1$ is given by

$$Q_1 \propto \phi_i (1 - \phi_i) (b_D - b_H)^2$$

(5.2)

where $\phi_i$ and $b_i$ are the volume fraction and scattering length, respectively, of the $i$th phase. In a two phase system with an interfacial region, i.e., diffuse boundaries, the invariant corrected for the influence of the interfacial region is given by

$$Q_1 = \frac{\int_0^\infty IQ^2 dQ}{\int_0^\infty [1 - E^2 Q^2 / 12]}$$

(5.3)

where $E$ is thickness of interfacial region. The corrected invariant defined by equation (5.3) gives an estimate of the mixing degree within the phase irrespective of mixing at the interfacial region. In the event of demixing process or phase dissolution, the volume fractions of the two components will necessarily change. However, mathematically, the change in the magnitude of $\phi_i (1 - \phi_i)$ will be small. Thus, the changes in the invariant $Q_1$ generally lead to associated changes in scattering length difference $(b_D - b_H)^2$. Therefore, the invariant $Q_1$ can be used to describe the demixing extent and demixing kinetics. An increase in the invariant $Q_1$ means an increase in the demixing degree.

The invariant $Q_1$ can be calculated in a straightforward manner discussed above for unoriented systems, but computation for perfectly or preferentially oriented systems requires assumptions about the form of the orientation distribution. The total scattered
intensity recorded by the area detector may provide an index to this quantity[7]. Shibayama and Hashimoto[8] have theoretically derived a small angle x-ray scattering from diblock polymer films which have a high degree of orientation on the basis of a preferentially oriented one-dimensional paracrystal model. The orientation distribution was assumed to be given by the Gaussian function. It has been demonstrated that the scattered intensity along the lamellar normal from perfectly oriented systems is proportional to the observed intensity at a given azimuthal angle multiplied by \( Q^2 \) (the Lorentz factor) on the basis that scattering profiles are obtained with point collimation and the lateral dimension of domains are much greater than their thickness. Therefore, the normalized integrated intensity along wavevector has the same form as that of an unoriented system.

It has been known that for a complex, low mobility system, the transition from one equilibrium state to another due to changes of thermodynamic variables can be considered as a relaxation process. The equation of relaxation can be expressed as

\[
Y = \frac{x_\infty - x_t}{x_\infty - x_0} = \exp\left(-\frac{t}{\tau}\right)
\]

where \( x \) is a physical quantity characteristic of systems, \( x_\infty, t, \) and \( x_0 \) denote the time at \( \infty, t, \) and \( 0, \) and \( \tau \) is the relaxation time. A relaxation equation with a double-relaxation time could also have been used[6,9-10]. However, models with a second relaxation time introduce more parameters. Because a single exponential has sufficed adequately in the present case, we here use fittings with a single relaxation time.

In our study, the invariant is used as a quantity \( x_t \) in equation (5.4) and the relaxation process of the demixing in C30/C36 pairs is phenomenologically described. We here are only concerned with an overview of the demixing toward the final equilibrium by using the invariant \( Q_1 \) as a physical quantity. The relaxation time \( \tau \) is used as a direct measure of the speed of changing process and, of course, of molecular motion. The half-time \( t_{1/2} \) corresponding to \( Y_{1/2} \) is equal to \( \tau \ln 2[4] \).
5.3 RESULTS AND DISCUSSION

5.3.1 COMPOSITION DEPENDENCE OF THE DEMIXING

Figure (5.1) presents the invariant as a function of annealing time for several \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixtures at 27°C. The invariant data exhibit a gradual increase with annealing time, implying an increase in the demixing with time. Since the first scattering patterns were collected at 30 minutes after quenching, curve shapes we observe would represent intermediate and later times of the demixing. The curve shapes are found to be the composition dependence. For the 1:4 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture, the invariant is initially steep, but then appears to level off at about 300 minutes. The tendency of the level-off seems to appear earlier for the 1:9 mixture. For the 1:1 mixture, however, the curve increases monotonically and no level-off is observed within the time scale of the experiments. The curve shape of the 3:8 mixture is between 1:1 and 1:4 mixtures. The results qualitatively show that in the concentration ranging from 1:1 to 1:9, the time...
TABLE 5.1 Relaxation times of $C_{30}H_{62}/C_{36}D_{74}$ mixtures at 27°C

<table>
<thead>
<tr>
<th>$C_{30}H_{62}/C_{36}D_{74}$</th>
<th>1/1</th>
<th>3/8</th>
<th>1/4</th>
<th>1/9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxation Time(±15)(min)</td>
<td>600</td>
<td>520</td>
<td>260</td>
<td>145</td>
</tr>
</tbody>
</table>

Figure (5.2) The composition dependence of relaxation time based on results presented in figure (5.1). The error limit is ±15 min.

required for the sample more unbalanced in concentration to reach an equilibrium is shorter than that for less unbalanced.

Solid lines in figures (5.1) are model fits to the data with equation (5.4). Figure (5.2) shows the plot of the relaxation time $\tau$ as a function of composition at 27°C. The $\tau$ is found to decrease with increasing the molar fraction of the longer chain in the range of composition investigated, quantitatively indicating that the demixing rate is faster for higher fractions of the longer chain than that for lower fractions.

We have noted that Basson and Reynhardt[11] have recently proposed a model in which two motions of molecules in a binary paraffin mixture at the low temperature orthorhombic phase are suggested. The first motion is the end-gauche defect motion of a longer chain, while the second motion is that a shorter chain executes a twofold screw motion of the entire chain around its axis. The vacancies created by the chain length mismatch can lower the potential barrier between all-trans and gauche conformations and therefore increase the probability that longer chains will be disorder orientations. The probability that a shorter chain will be in the translational position depends on the composition and temperature. If the fraction of longer chains is large, the energy for the
defect motion of longer chains increases due to an increase in intermolecular interactions between longer chains. This will lead to a longer relaxation time. On the other hand, however, longer chains have a low probability of occupying the longitudinal defect orientation, and therefore small fraction of shorter chains hide in lamellar matrixes will have a relatively unrestricted space in which they can execute screw motions. Such causes a shorter relaxation time. If the fraction of longer chains is small, the interaction between longer chains will decrease while the high probability that longer chains are in the longitudinal defect orientation will limit the size of vacancies and therefore offer a relatively restricted space to the longitudinal motion of shorter chains.

5.3.2 TEMPERATURE DEPENDENCE OF THE DEMIXING

The time evolution of the invariant at different annealing temperatures for the 1:4 \( C_{30}H_{62}/C_{36}D_{74} \) mixture is shown in figure(5.3). Also, the temperature dependence of curve shape is observed and seems to be more significant than the composition dependence. Similarly, the results show that the time required for the sample at higher temperatures to reach an equilibrium would be shorter than that at lower temperatures. It is consistent with the feature in scattering pattern themselves, as seen previously.

The temperature dependence of relaxation time \( \tau \) is plotted in figure(5.4) for the 1:4 \( C_{30}H_{62}/C_{36}D_{74} \) mixture. The results quantitatively indicate that the relaxation time \( \tau \) decreases with increasing annealing temperature in the range \( 26<T<41(\degree C) \) and therefore the demixing rate is faster at higher temperatures than that at lower temperatures. Also, the result is in agreement with changes in curve shapes. If it is assumed that the relaxation time \( \tau \) is given by the Arrhenius equation, we have

\[
\tau = \tau_0 \exp\left(\frac{E}{RT}\right)
\]

By plotting \( \ln \tau \) against \( 1/T \), as shown in figure(5.5), a good linear relation gives about 58KJ/mol for the apparent activation energy associated with a relaxation process in the 1:4 \( C_{30}H_{62}/C_{36}D_{74} \) mixture. The activation energy obtained is comparable to the result of Snyder et al[2a].
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Figure (5.3) The time dependence of the invariant for the 1:4 \(C_{30}H_{62}/C_{36}D_{74}\) mixture quenched from the melt to (a) 25°C, (b) 28.4°C, (c) 33°C, and (d) 41°C. Solid lines are calculated values with equation (5.4).

Figure (5.4) The temperature dependence of relaxation time for the 1:4 \(C_{30}H_{62}/C_{36}D_{74}\) mixture. The error limit is ±15 min.

<table>
<thead>
<tr>
<th>Annealing Temp. (°C)</th>
<th>25</th>
<th>26</th>
<th>27</th>
<th>28.4</th>
<th>33</th>
<th>41</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxation Time (±15)(min)</td>
<td>316</td>
<td>281</td>
<td>255</td>
<td>243</td>
<td>195</td>
<td>95</td>
</tr>
</tbody>
</table>
5.3.3 ISOTOPIC EFFECTS IN C30/C36 PAIRS

The isotopic effect on the demixing rate is investigated. Figure (5.6) shows the time dependence of invariant $Q_1$ for the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ and its reverse pair 1:1 $C_{30}D_{62}/C_{36}H_{74}$ quickly quenched from the melt to 20°C. The level-off is observed earlier for the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ than that for the 1:1 $C_{30}H_{62}/C_{36}D_{74}$. The relaxation times obtained are 580 min for the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ and 440 min for the 1:1 $C_{30}D_{62}/C_{36}H_{74}$, respectively. The results therefore indicate that the demixing rate of the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ mixture is faster than that of the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture and are in agreement with qualitative discussion of the isotopic effect on differences in the melting points and the volumes of pure components. On the basis of these differences, the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ mixture should separate faster than the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ because the differences in chain volumes and the melting points between $C_{30}D_{62}$ and $C_{36}H_{74}$ are significantly larger than those between $C_{30}H_{62}$ and $C_{36}D_{74}$. It is noted that the demixing rate of the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture at 20°C is close to that at 27°C.

The time evolution of $Q_1$ quantity has given us the information of overall demixing rate. However, since the isotope effect causes a typical two-stage process of the demixing for the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ mixture, as stated previously, the question is how fast the separation of the two components from the cocrystallized state is. The investigation of the separation rate is therefore necessary. This discussion is still based on equation (5.4). Instead of the invariant, the scattered intensity at peak position of the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture is used a quantity $x_t$ in equation (5.4) for both mixtures.
Figure (5.6) The time dependence of invariant for (a) the 1:1 C₃₀H₆₂/C₃₆D₇₄ and (b) the 1:1 C₃₀D₆₂/C₃₆H₇₄ at 20 °C. Solid lines are calculated values with equation (5.4).

Figure (5.7) The time dependence of scattered intensity at Q=0.082 Å⁻¹ for (a) the 1:1 C₃₀H₆₂/C₃₆D₇₄ and (b) the 1:1 C₃₀D₆₂/C₃₆H₇₄ at 20 °C. Solid lines are calculated values with equation (5.4).

Figure (5.8) The time dependence of scattered intensity at Q=0.136 Å⁻¹ for (a) the 1:1 C₃₀H₆₂/C₃₆D₇₄ and (b) the 1:1 C₃₀D₆₂/C₃₆H₇₄ at 20 °C. Solid lines are calculated values with equation (5.4).
Figure (5.7) shows the time dependence of scattered intensity at \( Q = 0.082 \, \text{Å}^{-1} \) for the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) and the 1:1 \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) at 20°C. Solid lines are calculated values with equation (5.4). The relaxation times obtained are 850 min for the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) and 680 min for the 1:1 \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \), indicating that the separation rate of the 1:1 \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \) mixture is also faster than that of the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture. The results seem to be in agreement with the conclusion that the time required for the sample more unbalanced in concentration to reach an equilibrium is shorter than that less unbalanced.

Although the statistics of counting limit the accuracy here the scattered intensities at \( Q = 0.136 \, \text{Å}^{-1} \) corresponding to that expected for the lamellar long spacing of pure C36 may also be analysed using equation (5.4). Figure (5.8) shows the fitting results. The approximate relaxation times for microcrystalline growth are 340 min for the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) and 115 min for the 1:1 \( \text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{74} \). Again, precipitating rate of enriched \( \text{C}_{36}\text{H}_{74} \) is faster than that of enriched \( \text{C}_{36}\text{D}_{74} \).

### 5.3.4 Wavevector Dependence of the Demixing

The \( Q_1 \) quantity has given us the information of overall variation of the demixing process with annealing time. However, since the demixing would involve different structural scales, it is necessary to investigate the time dependence of scattered intensity at different \( Q \) values.

![Figure (5.9)](image-url) The \( Q \) dependence of the relaxation time for (a) the 1:1 \( \text{C}_{36}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) and (b) the 1:4 \( \text{C}_{36}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) at 27°C. The error limit is ±10 min.
Figure 5.9 shows representative plots of the relaxation time as a function of wavevector $Q$ for 1:1 and 1:4 mixtures at 27°C. For the 1:1 mixture, the relaxation time is independent of $Q$ in the range of $Q<0.07\,\text{Å}^{-1}$ within the uncertainty of experiments and then decreases dramatically. For the 1:4 mixture, however, the relaxation time is found to show the $Q$ dependence in whole $Q$ range investigated. These results would indicate that the kinetics of the demixing undergoes different structural scales with a strong aggregation effect, i.e., smaller and unstable clusters of different length scales do aggregate together in the later stages of the demixing. The results may also show that within the time scale of the experiments, the size distribution of clusters in the 1:4 mixture could be slightly broader than that in the 1:1 mixture. Figure 5.10 shows plots of the relaxation time as a function of $Q$ for the 1:4 $\text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74}$ mixture at different annealing temperatures. The relaxation time values are found to show weaker $Q$ dependence at higher temperatures. If we recall that the demixing rate is faster and the average domain size is larger at higher temperatures, weaker $Q$ dependence would mean that at the same time scale, cluster sizes of the minor component in the mixture have reached an equilibrium already. Thus, it is again demonstrated that at higher temperatures the demixing rate is faster and the size distribution of clusters of minority component is relatively uniform.

Figure 5.11 shows the $Q$ dependence of the relaxation time for C30/C36 pairs at 20°C.
For the 1:1 C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}D\textsubscript{74} mixture, the relaxation time increases until reaching $Q=0.07\text{Å}^{-1}$ and then decreases as increasing $Q$. For the 1:1 C\textsubscript{30}D\textsubscript{62}/C\textsubscript{36}H\textsubscript{74} mixture, the relaxation time is independence of $Q$ in the range of $Q<0.07\text{Å}^{-1}$ within the uncertainty of experiments and then decreases. Similarly, the results may indicate that the size distribution of clusters in the 1:1 C\textsubscript{30}D\textsubscript{62}/C\textsubscript{36}H\textsubscript{74} mixture could be narrower than that in the 1:1 C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}D\textsubscript{74} mixture. We also note that for the 1:1 C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}D\textsubscript{74} mixture, the size distribution of clusters at 20°C could be broader than that at 27°C.

**Figure (5.11)** The $Q$ dependence of the relaxation time for C\textsubscript{30}/C\textsubscript{36} pairs at 20°C. $\bigcirc$: 1:1 C\textsubscript{30}D\textsubscript{62}/C\textsubscript{36}H\textsubscript{74}; $\bullet$: 1:1 C\textsubscript{30}H\textsubscript{62}/C\textsubscript{36}D\textsubscript{74}. The error limit is ±30 min.

### 5.3.5 Power-Law Behavior of the Demixing Kinetics

The investigations of the demixing process, including nucleation, spinodal decomposition, coarsening, and Ostwald ripening in mixtures quickly quenched from a one phase region to a two phase region, have received a great attention as part of a wide effort to examine nonequilibrium phenomena. One of the most important subjects in this field is the dynamic scaling of demixing processes.

A general prediction of models of the demixing process is that as a system approaches an equilibrium from an initial nonequilibrium disordered state after a quench, the growth of the average size $L$ obeys a power-law[1]
which contains few general parameters and does not depend on details of systems. The exponent $\alpha$ in equation (5.6) classifies a system into different growth classes. The value of $\alpha$ can vary from 0 to 1/2. However, it has been found that for systems with nonconserved order parameter (NCOP), $\alpha = 1/2$ (curvature-driven growth) [12] and that for conserved order parameter (COP), $\alpha = 1/3$ (Lifshitz and Slyozov growth) [13]. $\alpha = 1/3$ was first suggested for small volume fraction of one of the phases [13]. Recently, $\alpha = 1/3$ is also established for finite volume fraction when the two phases occupy comparable amounts [14]. In the Lifshitz-Slyozov evaporation-condensation mechanism of phase separation of an AB-mixture, the smaller clusters of B-rich phase become larger in an A-rich background. Binder and Stauffer [15] proposed an alternative mechanism to explain scaling behavior of phase separation. In their domain-diffusion and coalescence mechanism, $\alpha$ is 1/5, smaller than the value of the Lifshitz-Slyozov mechanism. The Monte Carlo Ising model [16] yields $\alpha$ values in the range 0.21-0.25. The exponents obtained experimentally vary considerably from one system to another, and even for a given system with a change in temperature. The values of $\alpha$ are often comparable to the theoretical ones but are also much lower than expected.

Here we assume that the invariant is proportional to the average ordered size $L$

$$L \propto t^\alpha \quad (5.6)$$

where $D$ is dimension. For a paraffin mixture, $L$ should be the average lateral dimension of domains. Thus, the kinetics of demixing processes can be displayed in terms of $\log Q_1$ versus log$t$. A more meaningful power-law will be examined.

Figure (5.12) (right hand side) shows $\log Q_1$ versus log$t$ plots for several $C_{36}H_{62}/C_{36}D_{74}$ mixtures quickly quenched to 27°C. For 1:1 and 3:8 mixtures, the curves show flat regions and then turn upwards while straight lines are observed for 1:4 and 1:9 mixtures. Values of $\alpha$ are obtained by the least-squares method and are listed in table 5.3. Since there are two linear regions for 1:1 and 3:8 mixtures, the values of $\alpha$ are determined only from longer time regions. If it is assumed that the growth of domains is one dimension, $D=1$, i.e., only along lateral direction, the $\alpha$ values obtained are in the range 0.24-0.35,
Figure (5.12) Log-Log plots of $Q_1$ versus $t$ for $C_{30}H_{62}/C_{36}D_{74}$ mixtures: (right) are (a) 1:1, (b) 3:8, (c) 1:4, and (d) 1:9 at 27°C; 1:4 mixture (left) at (a) 25°C, (b) 30°C, (c) 33°C, and (d) 41°C.

**Table 5.3** α values obtained from figure (5.12)

<table>
<thead>
<tr>
<th>$C_{30}H_{62}/C_{36}D_{74}$</th>
<th>1/1</th>
<th>3/8</th>
<th>1/4</th>
<th>1/9</th>
</tr>
</thead>
<tbody>
<tr>
<td>α (±0.03)</td>
<td>0.35</td>
<td>0.29</td>
<td>0.26</td>
<td>0.24</td>
</tr>
</tbody>
</table>

**Table 5.4** α values obtained from figure (5.12)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>25</th>
<th>30</th>
<th>33</th>
<th>41</th>
</tr>
</thead>
<tbody>
<tr>
<td>α (±0.03)</td>
<td>0.29</td>
<td>0.29</td>
<td>0.28</td>
<td>0.24</td>
</tr>
</tbody>
</table>

depending on the composition. Figure (5.12) (left hand side) also shows plots of log $Q_1$ versus log $t$ for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture quickly quenched to chosen temperatures. Straight lines are observed except for 41°C at which the curve shows a tendency to level.
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off. The values of $\alpha$ obtained are listed in table 5.4. The value $\alpha$ obtained from 41°C may contain uncertainty due to the curvature.

The study was extended to test the isotopic effect on the parameter $\alpha$. Figure (5.13) shows plots of log$Q_1$ versus log$t$ for 1:1 C30/C36 pairs quickly quenched to 20°C. In the similar time scale, the curve shapes show some differences. For the 1:1 C$_{30}$H$_{62}$/C$_{36}$D$_{74}$, the data shows curvature and then turns upwards while a line is observed for the 1:1 C$_{30}$D$_{62}$/C$_{36}$H$_{74}$. The greatest difference in kinetics behaviour is that the $\alpha$ value of the 1:1 C$_{30}$H$_{62}$/C$_{36}$D$_{74}$ is much larger than the corresponding reverse pair, as seen in table 5.5.

![Figure 5.13](image)

**Figure (5.13)** Log-log plots of $Q_1$ versus $t$ for 1:1 C$_{30}$/C$_{36}$ pairs at 20°C: (a) 1:1 C$_{30}$H$_{62}$/C$_{36}$D$_{74}$ and (b) 1:1 C$_{30}$D$_{62}$/C$_{36}$H$_{74}$.

<table>
<thead>
<tr>
<th>1:1 C$<em>{30}$H$</em>{62}$/C$<em>{36}$D$</em>{74}$</th>
<th>1:1 C$<em>{30}$D$</em>{62}$/C$<em>{36}$H$</em>{74}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.31$ (a)</td>
<td>$0.18$ (a)</td>
</tr>
<tr>
<td>$0.30$ (b)</td>
<td>$0.38$ (b)</td>
</tr>
</tbody>
</table>

(a) in terms of the invariant; (b) in terms of the intensity

We can qualitatively discuss the demixing in terms of the parameter $\alpha$. However, the question is whether the $\alpha$ values obtained from plots of log$Q_1$ versus log$t$ are the same as those from original definition, i.e., from plots of log$L$ versus log$t$. On the other hand, we hope that the parameter $\alpha$ can reflect the intrinsic feature of the demixing.

Accordingly, the power-law of scattered intensity is tested.

$$I \propto t^{\alpha}$$  \hfill (5.8)
For two dimension growth, $D=2$, the power-law of scattered intensity has been theoretically demonstrated [17-18]. The factor 2 arises because the peak intensity is proportional to the square of the average domain size, $L$, throughout a demixing process. If we accept this scaling law, the peak intensity can be used to determine $\alpha$. For present system, the growth dimension is assumed to be one, as we have already done.

Figure (5.14) Log-Log plots of $I$ versus $t$ for several $C_{30}H_{62}/C_{36}D_{74}$ mixtures: compositions at 27°C (right) are (a) 1:1, $Q=0.071Å^{-1}$, (b) 3:8, $Q=0.075Å^{-1}$, (c) 1:4, $Q=0.028Å^{-1}$, and (d) 1:9, $Q=0.028Å^{-1}$; the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture (left) at: (a) 25°C, (b) 30°C, (c) 33°C, and (d) 41°C.

Figure (5.14) (right hand side) shows plots of log$I$ versus log$t$ for different $C_{30}H_{62}/C_{36}D_{74}$ compositions quickly quenched to 27°C. The wavevectors we use are $0.071Å^{-1}$ for 1:1, $0.075Å^{-1}$ for 3:8, and $0.028Å^{-1}$ for 1:4 and 1:9. All $Q$ values are near the peaks corresponding to maximum intensity. Figure (5.14) (left hand side) also shows plots of log$I$ versus log$t$ for the 1:4 mixture quickly quenched to chosen temperatures. The curve
shapes observed are similar to those in figure (5.13). The \( \alpha \) values are determined in the same time ranges as those in figure (5.13) and are summarized in tables 5.6 and 5.7. As seen from tables, the values of \( \alpha \) obtained from equation (5.8) are larger than those from equation (5.7). It should be pointed out that unlike the invariant \( Q_1 \), the intensity power-law only indicates the separation of \( \text{C}_{30}\text{H}_{62} \) and \( \text{C}_{36}\text{D}_{74} \) components from coexisting state.

### TABLE 5.6 \( \alpha \) values obtained from figure (5.14)

<table>
<thead>
<tr>
<th>( \text{C}<em>{30}\text{H}</em>{62}/\text{C}<em>{36}\text{D}</em>{74} )</th>
<th>1/1</th>
<th>3/8</th>
<th>1/4</th>
<th>1/9</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) (±0.03)</td>
<td>0.63</td>
<td>0.54</td>
<td>0.52</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### TABLE 5.7 \( \alpha \) values obtained from figure (5.14)

<table>
<thead>
<tr>
<th>( T(°C) )</th>
<th>25</th>
<th>26</th>
<th>30</th>
<th>33</th>
<th>41</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) (±0.03)</td>
<td>0.60</td>
<td>0.62</td>
<td>0.60</td>
<td>0.58</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The isotope effect on the parameter \( \alpha \) is also tested. Figure (5.15) shows plots of \( \log I \) versus \( \log t \) for \( \text{C}_{30}/\text{C}_{36} \) pairs quickly quenched to 20°C. The values of \( \alpha \) are listed in table 5.5. The comparisons empirically indicate that for present system, the invariant power-law can not be applicable for the prediction of growth mechanisms as the system approaches the equilibrium after quenching.

![Log-Log plots of I at Q=0.071 A⁻¹ versus t for 1:1 C30/C36 pairs at 20°C: (a) the 1:1 C30H62/C36D74 and (b) the 1:1 C36D62/C36H74.](image)

For some systems, log-log plot curves of whole demixing process can be sketched as a common S-shaped curve or a parabolic shape \([2a,19-20]\). Snyder et al \([2a]\) suggested a common S-shaped curve for binary paraffin mixtures. Figure (5.16) hypothetically
Figure (5.16) A sketch of S-shaped log$L$ versus log$t$ curve representing log-log curves observed in experiments shows this common curve which is consistent with a mechanism in which domains grow to a certain size and thereafter the order develops much more slowly.

The curve is divided into 3 regions: A, B, and C, depending on the time evolution. The region A, where many small domains will be nucleated, is very short after the quench. The scattered intensity in the region A is weak and the peak is broad. In the region B, the domain growth occurs; smaller domains begin to incorporate into larger ones. The scattered intensity becomes stronger and the peak turns to be narrower. The average domain size reaches an equilibrium in the region C, where the scattered intensity will further increase mainly due to an ordering of lamellae. The exponent $\alpha$ should be very small in the region A, the largest at intermediate stages of the region B, and then decreases at later stages of the region B. The exponent $\alpha$ is also very small in the region C although the reason is totally different from that in region A.

As seen from figures (5.12) and (5.14), almost all measurements on C30/C36 pairs are not in the region A. The collected data should be in the region B within the time scale of the experiments. The curve shape and therefore value $\alpha$ may qualitatively reflect the rate of domain growth. For example, the lower $\alpha$ value of the 1:4 $C_{30}D_{62}/C_{16}H_{74}$ may imply that it separates faster and has approximated the region C within the time scale of the experiments. The $\alpha$ results here seem to be consistent with those obtained from relaxation calculations. However, the discussion of phase separation based on figure (5.16) could be too simple. The magnitude of $\alpha$, large or small, may indicate very complicated behaviour which need to be further discussed.
Except for the formation and growth of domains (or clusters), our SANS measurements indicate that the demixing process would involve an ordering process in lamellae, as stated above. The ordering occurs from the beginning of the demixing and lasts very long time. It influences the longitudinal diffusion of chains and therefore the demixing rate as well as the structure. A schematic model representing the defect motion which is considered to be of the most importance related to an ordering process appears in figure(5.17).

As known, the present system contains a lot of vacancies, including conformational defects, after quenching. All these vacancies are immobile laterally and can not mutually annihilate each other. They have to move only to chain end areas. The appropriate aggregation of defects can yield density deficient regions in chain end areas and locally approximate the conformation of transient ‘amorphous’, as shown in b and c of figure(5.17). The mobile defects can provide transient path for the chain migration. This may be an important factor that causes the demixing to be much faster (almost immediately) in a quenching sample than in a slow cooling sample (about two days). However, the aggregation of defects in domain boundaries may form a screen for demixing, which can cause a slow down of the demixing. After the initial ordering, the process would be associated with a better stretching of molecules and further elimination of defects both in ordered regions and in chain end areas. The existing deficient regions would partially incorporate into ordered lamellae. The domains would become larger and more order, and therefore the concentration of vacancies would decrease. As a consequence, the demixing rate would further decrease.
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It is useful at this point to compare our results with theoretical predictions. For the C_{30}H_{62}/C_{36}D_{74} mixture, our values of \( \alpha \) larger than \( 1/2 \) but seem to be close to the value of \( 1/2 \) of curvature-driven growth rather than classical \( 1/3 \) predicted by Lifshitz and Slyozov[13]. However, it is still very difficult to make a conclusion because obtained \( \alpha \) appears to regularly decrease as the mixture becomes significantly unbalanced in concentration. More serious problem concerns the smaller \( \alpha=0.38 \) for the 1:1 C_{30}D_{62}/C_{36}H_{74}. It is very close to \( 1/3 \) of Lifshitz-Slyozov mechanism.

The true growth behaviour in real materials and therefore \( \alpha \) value may be influenced by a number of effects[21] due to activated processes or the details of interaction potential, including impurities, random coupling or random fields, and second-phase particles. The \( \alpha \) is found to be sensitive to the existence of diffusing impurities[22], vacancies[23], quenched (immobile)[24] and annealed (mobile)[25] disordered or self-pinned effects[26]. Generally speaking, impurities, vacancies, and nonstoichiometry may reduce the \( \alpha \) values. Recently, experiments[27-28] have confirmed the reduction of \( \alpha \) due to the existence of impurities and nonstoichiometry. For paraffin mixtures, however, the most important effect on growth behaviour and \( \alpha \) values under experimental circumstances is vacancies. The movement and accumulation of vacancies have been schematically described above, as shown in figure(5.17). The ordering in systems with vacancies has been considered by Mouritsen and Shah(MS)[23]. Their computer simulations of ordering with mixed spin-flip and vacancies mechanism have shown that the \( \alpha \) value will change from \( 1/2 \) in an algebraic law to the smaller values in a logarithmic law due to annealed vacancies. As vacancies accumulate in domain boundaries, the direct interactions between domains become screened or even decoupled[23]. It means that the curvature-driven mechanism for pure systems becomes ineffective. In this case, the Lifshitz-Slyozov mechanism may be pertinent[29]. Also, Shah and Mouritsen[23] did not rule out the possibility that the dynamics may cross over to the Lifshitz-Slyozov law at later times. It should be pointed out that the crossover behaviour of the power-law proposed by Mouritsen and Shah[23] is actually associated with the fact that vacancies are only allowed to jump to nearest-neighbor positions. Very recently, Vives and Plane(VP) [30] have simulated a growth process in which vacancies jump both to next and to next-nearest neighbors. The vacancy jumps can accelerate the ordering process. Dynamics based on
the diffusion of a single vacancy gives rise to a $\alpha$ value larger than 1/2. The VP model may provide a more realistic process for understanding of the present system.

As discussed above, logarithmic growth may be a signature of the presence of vacancies. Figures (5.18) and (5.19) show plots of $I(Q,t)$ versus Log$t$ for the 1:4 mixture at different temperatures and for $C_{30}H_{62}/C_{36}D_{74}$ mixtures at 27°C, respectively. Over the range of times measured, it is apparent that the data are consistent with the logarithmic growth law. However, because the straight line is also obtained from the algebraic law in the same range of times for each case, figures (5.18) and (5.19) could not indicate the effect of vacancies on dynamics although somewhat improvement of linearity is observed at higher temperatures, 33°C and 41°C. Why both algebraic and logarithmic growth laws are obeyed for our data is so far unknown.

We have noted that for an Ising system with quenched, random impurities may show a following growth law[24]

$$L \propto [\text{Log}(t)]^m$$

(5.9)
A recent proposal[31] divides the kinetics of phase separation into four classes which are characterized by different low-temperature behaviour. Class 1 systems are similar to a simple Ising ferromagnet with spin-flip dynamics. In class 1 systems the domain size $L$ obeys familiar algebraic growth. The only difference in class 2 systems is that there are local defects which can cause freezing of the domain growth at absolute zero. Classes 3 and 4 have defects with domain size dependent activation energies. For classes 3 and 4, the domain size $L$ obeys a logarithmic growth. If $m=1$, systems belongs to class 3 which may contain the random-field Ising model. Class 4 has $m>1$, and may include dilute ferromagnets and spin glasses.

Figure(5.19) Plots of $I$ versus $\log t$ for (a) the 4:1 at $Q=0.0204\,\text{Å}^{-1}$, (b) the 1:1 at $Q=0.071\,\text{Å}^{-1}$, and (c) the 3:8 at $Q=0.078\,\text{Å}^{-1}$.

Figures(5.20) and (5.21) show plots of $\log I$ versus $\log(\log t)$ for the 1:4 $C_{36}H_{62}/C_{36}D_{74}$ at different temperatures and for different composition at $27^\circ\text{C}$, respectively. If the growth is assumed to be one dimension, the straight line fits give the exponents $m$ listed in Tables.
Figure (5.20) Plots of Log I at Q=0.028 A\(^{-1}\) versus Log(Logt) for the 1:4 mixture at (a) 26°C, (b) 30°C, (c) 33°C, and (d) 41°C.

| Table 5.8 m values obtained from figure (5.20) |
|-----------------|-----|-----|-----|-----|-----|
| T(°C)           | 25  | 26  | 30  | 33  | 41  |
| m(±0.03)        | 3.3 | 3.3 | 2.9 | 2.7 | 2.0 |

The m value is found to decrease with increasing temperature for a given composition. In the composition ranging from 1:1 to 1:9, the m value also decreases with increasing in composition. For 4:1 and 1:4 compositions, the m values are very close.

It is interesting to note that dependences of the exponent m on temperature and composition are comparable to the results obtained from previous relaxation analysis and...
Figure 5.21 Plots of Log I versus Log(Log t) for (a) the 4:1 at Q=0.0204 Å⁻¹, (b) the 1:1 at Q=0.071 Å⁻¹, (c) the 3:8 at Q=0.078 Å⁻¹, and (d) the 1:9 at Q=0.0204 Å⁻¹.

Table 5.9 m values obtained from figure 5.21

<table>
<thead>
<tr>
<th>Compounds</th>
<th>m (±0.03)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C30H62/C36D74</td>
<td>4/1</td>
</tr>
<tr>
<td>m (±0.03)</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Curves shapes of the time evolution of scattered intensity. The lower m value corresponds to the shorter relaxation time (or the faster demixing rate) and the earlier level-off of curves. These results seem show a relation between the molecular chain diffusion and the vacancy diffusion. In MS mode [23], if vacancy dispersion is static, the demixing will become pinned; if vacancies diffuse faster than molecular chains, the demixing will not be influenced by vacancies [23]. For present system, however, the situation is more complicated by the fact that the relaxation time depends on temperature and composition.
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We here suggest that whole demixing may be divided into two stages. The vacancies play double roles in the demixing. In the first stage mobile vacancies provide transient paths by which molecular chains can migrate. The vacancy jumps could accelerate the demixing[30]. In the second stage the accumulation of vacancies in boundaries could cause a slow down of the demixing. At the higher temperature, 41°C, more vacancies, including conformational defects, provide more chance for molecular diffusion, but, on the other hand, vacancies themselves may also move faster and accumulate in domain boundaries, as seen in figure(5.17). The shorter relaxation time may indicate the first stage while the level-off of the curve and the smaller m value may indicate the second stage. The first stage is dominant in the whole demixing process. At the lower temperature, 26°C, longer relaxation time may indicate a decrease in mobile vacancies, and no level-off of the curve within the time scale of the experiments as well as the larger m value may indicate that vacancies move slower and have not completely accumulated in boundaries.

Figure(5.22) Plots of Logl at Q=0.082Å⁻¹ versus Log(Lo guts) for (a) the 1:1 C₃₀H₆₂/C₃₆D₇₄ and (b) the 1:1 C₃₀D₆₂/C₃₆H₇₄ at 20°C.

Conclusively, the present results suggest that the demixing of present paraffin mixture belongs to class 4 and the system involves vacancies or defects with domain size dependent activation energies.
Figure (5.22) shows plots of LogI versus Log(Lo g t ) for the 1:1 C_{30}H_{62}/C_{36}D_{74} and 1:1 C_{30}D_{62}/C_{36}H_{74} mixtures at 20°C. The straight lines in the figure give m = 2.9 for the 1:1 C_{30}H_{62}/C_{36}D_{74} and m = 2.3 for the 1:1 C_{30}D_{62}/C_{36}H_{74}. The difference in the exponent m between C_{30}/C_{36} pairs may be again related to the difference in chain volumes of two components and therefore difference in the magnitude and number of vacancies.

It should be pointed out that there are no theories or simulations of the phase separation kinetics which can totally deal with the present system, as far as we know. For example, the computer simulations of Shah and Mouritsen [23] are restricted to the case where the boundary and the vacancy mobilities are comparable during the quench. However, our results really show that vacancies (or defects) and isotope effects play roles in demixing processes and change the exponents α and m.

5.4 DYNAMIC SCALING FUNCTIONS

When the dynamic scaling occurs, the process of phase separation can be understood to be entirely controlled by a unique characteristic length, ξ(t). A direct consequence of dynamic scaling is that the structure function S(Q,t) follows a simple asymptotic behavior at later stages of the phase separation. In practice, the first moment of the structure factor Q_{1}, or the wavevector Q_{m} corresponding to the maximum structure function, or the radius of gyration R_{g} could be chosen as a characteristic length. Such scaling behavior has now been found experimentally in many different systems and appears universal.

The purpose of this section is further to perform a quantitative test of the dynamic scaling hypothesis in C_{30}H_{62}/C_{36}D_{74} mixtures at several annealing temperatures as well as in one composition of the C_{30}D_{62}/C_{36}H_{74} mixture. We use the first moment of the structure factor, Q_{1}(t), as a measure of the inverse of the real space characteristic length in the investigation. Three scaling functions will be tested.

Moments of the structure factor S(Q,t) are defined as follows

\[ Q_{n}(t) = \frac{\sum Q^{n}S(Q,t)}{\sum S(Q,t)} \] (5.11)
which is found to behave quite smoothly with time\cite{13}. Phenomenological results and computer simulations suggest that the scaling function has a following form\cite{15,16,32,33}

$$S(Q,t) = J(t)F(Q_s(t))$$  \hspace{1cm} (5.12)

where $F(Q_s)$ is a time-independent scaling function and $J(t)$ is the scaling factor which is proportional to $\xi^v$.

$$S(Q,t) \propto \xi(t)^vF[Q_s(t)]$$  \hspace{1cm} (5.13)

The $S(Q,t)$ is directly measured by SANS techniques. The actual form of $F[Q_s(t)]$ is subject of recent interest. The general form depends on whether the order parameter is conserved or not.

### 5.4.1 MLK's Scaling Function

The scaling function in three dimensions ($v=3$) has been found by Marro, Lebowitz, and Kalos (MLK)\cite{16} from their computer simulations

$$F(x,t) = \frac{Q_1^2S(Q,t)}{\sum Q^2S(Q,t)} = Q_1^2S(Q,t)$$  \hspace{1cm} (5.14)

where $x=Q/Q_1$. As seen in equation (5.14), the first moment of the structure factor has been chosen as a characteristic length. The scaling function $F(x,t)$ is independent of time after an initial time period, e.g., $F(x,t)=F(x)$. The shape of scaling function $F(x)$ is found to be similar throughout different classes of substances\cite{34}. However, discrepancies have been reported in the case of a magnetic alloy\cite{35}. Our SANS data are also used to verify the validity of MLK's scaling function at later stages of the demixing.

In order to compare the experimental patterns with the scaling curves, figures (5.22) and (5.23) show the time evolution of the scattering patterns (plotted in the form of $IQ^2$) for 1:1 and 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixtures quickly quenched from the melt to 27°C. The experimental criterion for establishing “late stages” in terms of equation (5.14) is the time independence of $Q_2/Q_1^2$. The representative plots of $Q_2/Q_1^2$ versus $t$ are shown in figures (5.24) and
Figure (5.22) The time evolution of the IQ^2 versus Q for the 1:1 C_{30}H_{62}/C_{36}D_{74} mixture quickly quenched from the melt to 27°C. Annealing times from bottom to top are 30 min, 90 min, 150 min, 210 min, 270 min, 390 min, and 510 min.

Figure (5.23) Time evolution of the IQ^2 versus Q for the 1:4 C_{30}H_{62}/C_{36}D_{74} mixture quickly quenched from the melt to 27°C. Annealing times from bottom to top are 30 min, 90 min, 150 min, 210 min, 270 min, 330 min, 390 min, 450 min, 510 min, 570 min, and 630 min.
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Figure (5.24) Time dependence of the ratio $Q_2/Q_1^2$ for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture at a: 26°C and b: 33°C.

Figure (5.25) Time dependence of the ratio $Q_2/Q_1^2$ for 3:8 and 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixtures at 27°C.

As seen, the plots remain almost constants in corresponding time ranges. These figures are only meaningful to the extent that the first few moments of SANS data may be collected accurately. The scaling function is therefore calculated within the time range determined from the plot of $Q_2/Q_1^2$ versus $t$. 

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Figure 5.26 Ln-In plots of the scaling function F versus x=Q/Q₁ in terms of equation (5.14) for the 1:4 C₁₃H₆₂/C₁₃D₇₄ mixture quickly quenched from the melt to 27°C for (a) 1/1, (b) 3/8, and (c) 1/4.
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Figure (5.27) Ln-ln plots of the scaling function F versus x=Q/Q_1 in terms of equation (5.14) for the 1:4 C_{30}H_{62}/C_{36}D_{74} mixture quickly quenched from the melt to chosen temperatures: (a) 30°C, (b) 33°C, and (c) 41°C.
Figure (5.28) Plots of the $F\cdot(Q/Q_1)^2$ versus $x=Q/Q_1$ corresponding to figure (5.26)
Figure (5.29) Plots of the $F \cdot (Q/Q_1)^2$ versus $x=Q/Q_1$ corresponding to figure (5.27)
Figure (5.30) Plots of ln-ln (upper) and the $F^*(Q/Q_1)^2$ (down) versus $x=Q/Q_1$ for the 1:1 $C_{36}D_{62}/C_{36}H_{74}$ mixture quickly quenched from the melt to $20^\circ C$ at several times.

The scaling behavior of the experimental structure function has been examined in figure (5.26) for 1/1, 3/8, and 1/4 $C_{30}H_{62}/C_{30}D_{74}$ mixtures at $27^\circ C$. Figure (5.27) shows the scaling tests for the 1:4 mixture at $30^\circ C$, $33^\circ C$, and $41^\circ C$. We use the Ln-Ln plot of $[Q_1(t)]^3 \sum S(Q,t)/Q^2 S(Q,t)$ versus $x=Q/Q_1(t)$ for different lengths of time noted in figures. All curves look to be scaled together.

In order to test the scaling behaviour further, the data are plotted in a way of $F^*[Q/Q_1(t)]^2$ versus $x=Q/Q_1(t)$. This allows the whole shape of curves to be clearly seen.
Figures (5.28) and (5.29) show plots of $F[Q/Q_1(t)]^2$ versus $x=Q/Q_1(t)$ corresponding to figures (5.26) and (5.27), respectively. As can be seen, all curves fall almost precisely on top of one another for each case. The results unambiguously indicate that at these times the dynamic scaling is followed exactly within experimental errors of the data.

The scaling behavior was also tested for a reverse pair, the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ mixture. The results are shown in figure (5.30). The scaling validity of equation (5.14) is again demonstrated for the later stages of demixing. It is noted that the scattered intensity at $Q=0.135\AA^{-1}$ is independent of annealing time at the later stages.

### 5.4.2 PLKP'S SCALING FUNCTION

Phani, Lebowitz, Kalos, and Penrose (PLKP) (36) have proposed another scaling function to describe the kinetics of order-disorder transition by using computer simulations. The theoretical approach is based on a kinetic equation for the motion of domain walls separating domains with different orderings, which was independently proposed by Lifshitz[37] and by Cahn and Allen[38].

If the staggered structure factor $\bar{S}(Q,t)$ (36) has the same definition as that in equation (5.14), the scaling function $F(x)$ can be constructed as follows

$$F(x,t) = t^{-3/2}S(Q,t) = \frac{t^{-3/2}S(Q,t)}{\sum Q^2S(Q,t)}$$  \hspace{1cm} (5.15)

where $x=Qt^{1/2}$. The way of deciding whether there is scaling behaviour is the similar to that in terms of equation (5.14). If curves of $F(x,t)$ versus $x=Qt^{1/2}$ can be superposed so that they overlap exactly, there is scaling behaviour.

The general validity of equation (5.15) is demonstrated for the SANS data obtained from different experimental conditions. Figure (5.31) shows the plots of $\log F(x,t)$ versus $x=Qt^{1/2}$ for five compositions quickly quenched from the melt to $27^\circ$C. The plots of $\log F(x,t)$ versus $x=Qt^{1/2}$ are shown in figure (5.32) for the 1:4 mixture quickly quenched to different depths ($25^\circ$C, $30^\circ$C, $33^\circ$C, and $41^\circ$C). The scaling test for the 1:1 $C_{30}D_{62}/C_{36}H_{74}$
Figure 5.31 Plots of $\log\left[\frac{S(Q,t)}{\sum S(Q,t)Q^2}\right] t^{-3/2}$ versus $x=Qt^{1/2}$ for $C_{30}H_{62}/C_{36}D_{74}$ mixtures: a: 4/1, b: 1/1, c: 3/8, d: 1/4, and e: 1/9 at 27°C.
Figure (5.32) Plots of $\log[S(Q,t)/\sum S(Q,t)Q^2]t^{-3/2}$ versus $x = Qt^{1/2}$ for the 1:4 $C_{36}H_{62}/C_{36}D_{74}$ mixture at: a) $25^\circ C$, b) $30^\circ C$, c) $33^\circ C$, and d) $41^\circ C$. 
Figure (5.33) Plots of $\log [S(Q,t)/\sum S(Q,t)Q^2]t^{-3/2}$ versus $x=Qt^{1/2}$ for a: the 1:1 $C_{30}D_{62}/C_{36}H_{74}$ and b: the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture at 20°C.

is shown in figure (5.33). As seen in these figures, the scaling behaviour predicted by equation (5.15) is excellently obeyed. Although the scaling function is calculated in a range $0.020<Q/\AA^{-1}<0.055$, the scaling behaviour is observed in a very wider $Q$ range and should be independent of $Q$. It is interesting to note that for our SANS data the equation (5.15) can predict the scaling behaviour in whole time scale of the experiments. The scattering patterns at annealing times which should not be considered as "later stages" according to the criterion of equation (5.12) are also scaled in terms of equation (5.15).

5.4.3 FLPA'S SCALING FUNCTION

The demixing kinetics of paraffin mixtures is also described by the third scaling function.
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proposed by Fratzl, Lebowitz, Penrose, and Amar (FLPA)\[39-40\]. The discussion of universal features of this scaling function is based on a two-phase model: a mixture of two types of domains separated by thin interfaces. The scaling function $L_v(x)$ in FLPA's formula\[39-40\] is the normalized structure factor in a two phase system for $v$-dimension.

For three dimensions, the scaling function $L_v$ has a simple analytical form\[39-40\]

\[
L_v(x) = \frac{a_v x^4}{x^4 + c_v}
\]

\[
P_3(x) = \frac{b_3}{b_3 + (x^2 - 1 + d_3)^2}
\]

\[
b_3 = \frac{4\gamma^2}{(1 - \gamma^2)^2}(1 - d_3)
\]

\[
c_3 = \frac{d_3}{b_3 - d_3(1 - d_3)}
\]

\[
a_3 = (1 + c_3)(1 + \frac{d_3^2}{b_3})
\]

where $x = Q/Q_m$. As seen from the definition of equation (5.16), the maximum value of $L_v$ should be 1 at $x = 1$. Many experimental data have been well fitted with equations from (5.16) to (5.20)\[39\]. It is empirically found that $d_3$ is given an universal value 0.06 for all cases\[39\]. In the following, we construct the scaling function by using $Q_1$ as real space characteristic length rather than $Q_m$ and test the scaling behaviour. The quantity $x = Q/Q_m$ in equation (5.16) is therefore replaced by $x = Q/Q_1$. In calculations, we accordingly fix the parameter $d_3 (=d)$ to 0.06 and leave $\gamma$ as an only adjustable parameter for the fitting of scaling function.

Figure (5.34) shows scaling functions with different $\gamma$ for 1:1 and 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixtures quickly quenched from the melt to 27°C. The peak width of the scaling function becomes narrower as $\gamma$ is decreased. The maximum values $L_v$ really occur when $x = 1$ but is found to be smaller than 1 when $\gamma$ is decreased to the same extent. Figure (5.35) shows plots of peak maximum (PM) as a function of $\gamma$ for several compositions and the data are summarized in table 5.10. From the definition of equation (5.16), the $\gamma$ value should be 1. Accordingly, there are many choices of $\gamma$ for a given composition. We here choose the $\gamma$
value which corresponds to the peak maximum only marginally smaller than 1. These data are: \( \gamma = 0.65 \), \( PM = 0.998 \) for 4:1; \( \gamma = 0.30 \), \( PM = 0.998 \) for 1:1; \( \gamma = 0.40 \), \( PM = 0.998 \) for 3:8; \( \gamma = 0.65 \), \( PM = 0.995 \) for 1:4; and \( \gamma = 0.85 \), \( PM = 0.998 \) for 1:9.

**TABLE 5.10** values of PM at different \( \gamma \) for \( \text{C}_30\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) at room temperature

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<th>H/D</th>
<th>( \gamma )</th>
<th>0.13</th>
<th>0.2</th>
<th>0.3</th>
<th>0.40</th>
<th>0.55</th>
<th>0.65</th>
<th>0.85</th>
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<tr>
<td>4/1(570min)</td>
<td>Peak Maximum</td>
<td>0.895</td>
<td>0.943</td>
<td>0.974</td>
<td>0.991</td>
<td>0.995</td>
<td>0.998</td>
<td>1.0</td>
</tr>
<tr>
<td>1/1(630min)</td>
<td>Peak Maximum</td>
<td>0.994</td>
<td>0.997</td>
<td>0.998</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>3/8(750min)</td>
<td>Peak Maximum</td>
<td>0.987</td>
<td>0.995</td>
<td>0.997</td>
<td>0.998</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>1/4(630min)</td>
<td>Peak Maximum</td>
<td>0.794</td>
<td>0.875</td>
<td>0.940</td>
<td>0.969</td>
<td>0.988</td>
<td>0.995</td>
<td>1.0</td>
</tr>
<tr>
<td>1/9(330min)</td>
<td>Peak Maximum</td>
<td>0.617</td>
<td>0.794</td>
<td>0.907</td>
<td>0.967</td>
<td>0.983</td>
<td>0.991</td>
<td>0.998</td>
</tr>
</tbody>
</table>

The question is whether the validity of scaling function is influenced by the parameter \( \gamma \). A set of \( \gamma \) values corresponding \( PM = 1 \) are therefore chosen to fit the scaling function. The representative results are shown in figure (5.36) for the 1:1 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture and in figure (5.37) for the 1:4 \( \text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74} \) mixture at room temperature. As seen, all curves are excellently scaled together. The same conclusion is obtained for other compositions. The results indicate that the validity of scaling function is independent of \( \gamma \), at least for our data, in meaningful ranges of equation (5.16). The \( \gamma \) depends on composition, however. Especially, \( \gamma \approx 0.3 \) for the 1:1 mixture is comparable to that for all critical
Figure (5.35) Plots of peak maximum as a function of $\gamma$ for (a) 4/1 in 570 min, (b) 1/1 in 630 min, (c) 1/4 in 630 min, and (d) 1/9 in 330 min at room temperature.

quenches in the literature [39]. We also note that the scaling behaviour predicted by equation (5.16) is observed in the whole time scale of the experiments. Similarly, figure (5.38) shows scaling functions for the 4:1 mixture with $\gamma = 0.65$ and for the 1:9 mixture with $\gamma = 0.85$ at 27°C. Again, all curves fall precisely on the top of one another for
Figure 5.36) Scaling functions of three dimensions for the 1:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture at 27°C with (a) $\gamma=0.3$ and (b) $\gamma=0.6$.

Figure 5.37) Scaling functions of three dimensions for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture at 26°C with (a) $\gamma=0.65$ and (b) $\gamma=0.75$.

Each case. Figure 5.39 shows the scaling functions with $\gamma=0.65$ for the 1:4 mixture at different temperatures. The values of peak maximum are listed in Table 5.11. The results are in agreement with the computer simulations [39-40] that the scaling function does not depend on the temperature for a given composition.
Figure (5.38) Scaling functions of three dimensions for (a) the 4:1 $C_{30}H_{62}/C_{36}D_{74}$ mixture with $\gamma=0.65$ and (b) the 1:9 $C_{30}H_{62}/C_{36}D_{74}$ mixture with $\gamma=0.85$ at 27°C.

Figure (5.39) Scaling functions of three dimensions for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture at different annealing temperatures and times with $\gamma=0.65$.

| TABLE 5.11 Peak maximum at $\gamma=0.65$ for the 1:4 mixture |
|-----------------|-----|-----|-----|-----|
| $T(°C)$         | 41  | 33  | 30  | 26  |
| Peak Maximum    | 0.997| 0.994| 0.995| 0.995 |
Figure (5.40) Plots of peak maximum as a function of $\gamma$ for the 1:1 $\text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{72}$ mixture in 1050 min at 20°C.

Figure (5.41) Scaling functions of three dimensions for the 1:1 $\text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{72}$ mixture at 20°C with $\gamma = 0.4$.

The validity of the scaling function is also tested for the 1:1 $\text{C}_{30}\text{D}_{62}/\text{C}_{36}\text{H}_{72}$ mixture. Figure (5.40) shows the plot of peak maximum versus $\gamma$ in 1050 min after quenching. The $\gamma = 0.4$ is chosen. Figure (5.41) shows plots of $L(x)$ versus $x$. Once again, the scaling behaviour predicted by equation (5.14) is exactly obeyed.

At large $x$ the equation (5.16) should have behaviour in agreement with Porod’s law. A representative plot of $\log L$ versus $\log x$ is shown in figure (5.42) for the 1:4 mixture in 630 min after quenching. The slope of -4 is indeed obtained in large $x$. Similar results are found for other data. Porod’s law is observed because in the late stages of demixing, the domain size is much larger than the thickness of the interfaces [40].
we have found general agreement between SANS experimental results and the predictions of FLPA's scaling function for paraffin mixtures investigated. The scaling function $L(x)$ is determined just by the volume fraction. For example, the $\gamma$ values for 1:1 and 1:9 mixtures are very different. The reason why the scaling function only depends on one parameter has been interpreted as a consequence that asymptotically self-similar ensemble of interface configuration is completely determined by the volume fraction [40], based on Pego's asymptotic analysis [41] of the Cahn-Hilliard model [42] and on the assumption of asymptotic self-similarity in a two-phase framework. However, it should be pointed out that for our data the dependence of the parameter $\gamma$ on composition indeed exists but not strongly for mixtures unbalanced in concentration. Another consistency check on the analysis of the experimental data is temperature independence of $\gamma$. We also note that the $\gamma$ values obtained from 1:4 and 4:1 mixtures are very close. This is because the volume fractions of minority components in these mixtures are not very different.

Fratzl and Lebowitz [39] have discussed a relationship between the parameter $\gamma$ and the morphology of a system, as shown in figure (5.43). Their results indicate that the higher values of $\gamma$ are related to a morphology with spherical clusters of minority component isolated in matrix of majority component, and the lower values of $\gamma$ predict the interconnected morphology with mainly by rods or by plates. As stated by Fratzl et al. [40], clusters are not completely spherical because of the anisotropy of the surface tension according to the Ising model. It can be seen that our results are not completely predicted by FL map. However, if we insist on discussing the morphology in terms of figure (5.43), the 1:1 mixture could have an interconnected morphology composed mainly
by plates while the mixtures significantly unbalanced in concentration, for instance 4:1 and 1:9 mixtures, could have a morphology with clusters of minority components isolated in matrix of majority components.

5.5 CAHN'S MODEL

Cahn[43-44] derived a relation which describes the nucleation. A constant isotropic growth velocity is assumed in Cahn’s model. This model has been used to fit SAXS data for kinetics of the microphase separation and the ordering of a diblock copolymer[45].

In Cahn’s model[43], the scattered intensity at a fixed wavevector can be expressed as

\[ I(t) = I_\infty \{1 - \exp[-bf(t-t_0)]\} \]  

where

\[ f(t) = \frac{1}{a} \int_0^1 (1 - \exp[-\frac{\pi}{3a}(1 - 3x^2 + 2x^3)])dx \]  

Figure(5.43) The plot of parameter \( \gamma \) as a function of volume fraction, indicating the relationship between \( \gamma \) and morphology[Fig(2) in ref.39 and Figure(1) in ref.40].
and parameters a and b here are related to the growth velocity, the surface area available for nucleation, and the state-state nucleation rate[43-44]. The ratio of a to b is found to play a role of an effective time constant[45]. At early times or late times, the equation (5.21) can be reduced to the Mehl-Johnson-Avrami equation[44,46,47] with \( f(t) \propto t^4 \) or \( f(t) \propto t \), respectively. The nucleation rate here is approximated as a step function which is zero during the incubation time \( t_0 \) and a nonzero constant after \( t_0 \), as adapted by Harkless et al[45].

SANS data were fitted by Cahn’s model. Figure(5.44) shows comparisons between the experimental (open circle) and calculated (solid line) data for the 1:4 \( \text{C}_{30} \text{H}_{62}/\text{C}_{36} \text{D}_{74} \) mixture quickly quenched from the melt to 41°C at several Q values. Fittings were carried out by using a least-squares program with variable parameters a, b, and \( I_\infty \). As seen, Cahn’s model can fit the experimental data very well within the time scale of the experiments. Similar results are obtained for other data. It is found that the deviation between experimental and calculated data in short times at low-temperature, for example, at 26°C, is slightly larger than that at high-temperature.

In figures (5.45) and (5.46), the variation of the effective time \( \alpha/b \) with Q for the 1:4 \( \text{C}_{30} \text{H}_{62}/\text{C}_{36} \text{D}_{74} \) mixture at 26°C and 41°C are shown. The results show that the effective time \( \alpha/b \) initially decreases and then tends to level off to a constant with increasing wavevector. This implies that the demixing would form segregates with different sizes. The similar behaviour has been previously seen.

Figure(5.47) shows plots of the experimental and calculated data for the 1:4 \( \text{C}_{30} \text{H}_{62}/\text{C}_{36} \text{D}_{74} \) mixture quickly quenched to chosen temperatures. The wavevector is fixed at 0.0205Å\(^{-1}\). The changes in curve shape with time is quenching temperature dependent. Similar changes have been observed in plots of the invariant versus time. These observations suggest that, in view of the nucleation theory, there is a smaller free-energy difference at higher quenching temperatures. Figure(5.48) shows the plot of the effective time \( \alpha/b \) versus quenching temperature for the 1:4 mixture.
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Figure 5.44  Fits of Cahn’s model to data of the 1:4 C_{36}H_{62}/C_{36}D_{74} mixture quickly quenched from the melt to 41°C. Q values are: (a) 0.0127 Å⁻¹, (b) 0.0166 Å⁻¹, (c) 0.0205 Å⁻¹, (d) 0.0243 Å⁻¹, (e) 0.0282 Å⁻¹, and (f) 0.0359 Å⁻¹.
The effective time $a/b$ is found to decrease with increasing quenching temperature, as would be expected. If it is assumed that the effective time is given by the Arrhenius equation, we have

$$a/b = (a/b)_0 \exp(E/RT)$$

(5.23)

By plotting $\ln(a/b)$ against $1/T$, as shown in figure(5.49), a good linear relation gives about 65KJ/mol for apparent activation energy associated with the demixing in the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture. This value is comparable to 56KJ/mol determined from the previous analysis as well as the result of Snyder et al[2a].

![Figure(5.45)](image)

Figure(5.45) The plot of the effect time $a/b$ as a function of wavevector $Q$ for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture quickly quenched from the melt to 26°C. The error limit is ±15 min.

![Figure(5.46)](image)

Figure(5.46) The plot of the effect time $a/b$ as a function of wavevector $Q$ for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture quickly quenched from the melt to 41°C. The error limit is ±10 min.
Figure (5.47) Fits of Cahn's model to data of the 1:4 C₃₀H₆₂/C₃₆D₇₄ mixture quickly quenched from the melt to chosen temperatures: (1) 26°C, (2) 30°C, (3) 33°C, and (4) 41°C at Q=0.0205 Å⁻¹.

Figure (5.48) The plot of the effective time a/b as a function of temperature for the 1:4 C₃₀H₆₂/C₃₆D₇₄ mixture. The error limit is ±1.5 min.

Figure (5.49) The Arrhenius plot for the 1:4 C₃₀H₆₂/C₃₆D₇₄ mixture.
5.6 KINETICS OF TWO PHASE DISSOLUTION

There have been many theories and experiments on chain dynamics in condensed materials and concentrated solutions which involve the diffusion of compatible binary mixtures. de Gennes[48] proposed the reptation model whereby the polymer chain is forced to wriggle when the concentration of the polymer solution is high enough to cause dense chain entanglements. The translation diffusion coefficient of long, linear polymer chains in the randomly mixed state is inversely proportional to the square of molecular weight. By adapting the principle of the reptation model of de Gennes, Doi and Edwards[49] (DE) have developed a ‘tube theory’ in which the polymer chain moves by wriggling along its axis like a snake. The chain ends, like the head of a snake, are unconstrained, so that they can take any direction with equal probability. The tube theory reveals the important relationship between macroscopic viscoelastic relaxation behaviour and microscopic molecular diffusional phenomena. The DE model has been modified by Merrill et al[50] to describe the chain diffusion and relaxation in oriented media. In their model, local orientational correlations between segments of chain molecules are incorporated and chain ends escaping out of the tube move into an oriented medium with which polymer chains partially align. On the other hand, Summerfield and Ullman[51-52] have derived an equation for diffusional behavior of polymer molecules labeled by deuterium in an unlabeled matrix.

For stiff chains, for example, paraffins and liquid crystals, the chains tend to be parallel to each other during diffusion. When the tendency towards chain orientation is strong enough, the system will align along certain direction. The experimental works on the dynamics of stiff chains are comparatively few and there is little theory. Recently, Doi et al[53] derived a new dynamic equation for a concentrated solution of rod-like polymer by using a mean field approximation. This equation could be applied to both the isotropic and liquid crystalline phases. The rotation and translation of molecular chains are considered in the theoretical framework. The equation can also deal with the problems of spatial heterogeneity.
5.6.1 SUMMERFIELD-ULLMAN MODEL

According to Summerfield and Ullman [51-52], for a system initially composed of randomly mixed clusters of protonated and deuteriated species, the scattered intensity \( I(Q,t) \), after annealing time, can be expressed

\[
I(Q,t) = I(Q,\infty)[1 - \alpha(0,t) - \frac{1-\beta}{1-\varphi}\exp(-2\Gamma t)] + I(Q,0)\exp(-2\Gamma t)
\]

\[
= I(Q,\infty)[1 - \alpha(0,t)] + [I(Q,0) - \frac{1-\beta}{1-\varphi} I(Q,\infty)]\exp(-2\Gamma t)
\]

(5.24)

where \( \alpha(Q,t) \) is a correlation function defined by

\[
\alpha(r,t) = \frac{\left\langle c(r + r',t)c(r,t) \right\rangle}{\varphi - \varphi^2}
\]

(5.25)

where \( c(r,t) \) is the concentration of molecular centers of the deuteriated species at distance \( r \) and time \( t \), the average value of the deuteriated component is \( \varphi \). The angle brackets represent an ensemble average. \( \Gamma \) here is diffusion rate, and \( \varphi<\beta<1 \). If \( \beta=1 \), the initial stage is that of well-separated components; and equation (5.24) turns to be

\[
I(Q,t) = I(Q,\infty)[1 - \alpha(0,t)] + I(Q,0)\exp(-2\Gamma t)
\]

(5.26)

which is mathematically similar to the well-known Cahn-Hilliard-Cook [42] scattering equation originally proposed for spinodal decomposition of metals, as shown as follows

\[
I(Q,t) = I(Q,\infty)[1 - \exp(-2\Gamma t)] + I(Q,0)\exp(-2\Gamma t)
\]

\[
= I(Q,\infty) + [I(Q,0) - I(Q,\infty)]\exp(-2\Gamma t)
\]

(5.27)

But, a quite different physical meaning for these two equations has been discussed [51]. If \( \beta=\varphi \), the initial system is randomly mixed and the equation (5.24) can be rewritten as

\[
I(Q,t) = I(Q,\infty)[1 - \alpha(0,t) - \exp(-2\Gamma t)] + I(Q,0)\exp(-2\Gamma t)
\]

\[
= I(Q,\infty)[1 - \alpha(0,t)] + [I(Q,0) - I(Q,\infty)]\exp(-2\Gamma t)
\]

(5.28)

Equation (5.24) represents a situation between these two extremes. However, if a system is near equilibrium, \( \beta \) differs only slightly from \( \varphi \) and \( \alpha(0,0) \) is only marginally greater than zero. The relaxation time is inversely proportional to \( \Gamma \). The diffusion rate is assumed to be a form \( \Gamma=DO^2 \), where \( D \) is an apparent diffusion coefficient. For a temperature jump experiment, \( D \) is assumed to be negative which corresponds to a growth of concentration...
fluctuation.

In some temperature jump experiments, $I(Q,0)$ is much greater than $I(Q,\infty)$, and therefore $I(Q,\infty)$ is in practice assumed to be zero. In this case, equations (5.24) and (5.27) are exactly the same mathematically, which, however, does not necessarily mean that the scattering pattern behaviour should be interpreted as a spinodal decomposition.

5.6.2 RESULTS

The kinetics of the phase dissolution of long time ageing (near one year) 1:4 $\text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74}$ mixture are described by using Summerfield-Ullman model, as a first approximation. The equilibrium morphology of mixtures unbalanced in concentration after quick quenching has been schematically shown in figure (4.5.2.1). The oriented lamella of the minority component are suggested to be randomly distributed. The initial stage of the two components in aged 1:4 $\text{C}_{30}\text{H}_{62}/\text{C}_{36}\text{D}_{74}$ mixture is considered to be well-separated. The aged sample was rapidly heated to 46°C, which is just about 1°C above that at which the demixing occurs, as known previously, and annealed at this temperature for about several hours. The variation of the scattered intensity with annealing time indicates that the two phases are destroyed by molecular diffusion occurring entirely in the orthorhombic phase.

![Figure 5.50](image-url)

Figure(5.50) Plots of $\ln I$ versus $t$ for aged 1:4 mixture quickly heated to 46°C at $Q/\AA^{-1}$: 0.024, 0.028, 0.036, and 0.048.
Figure (5.50) shows representative semilogarithmic plots of $I(Q,t)$ versus $t$ for the 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture at different $Q$. For the aged sample, it is assumed that initial time is equal to 6 seconds instead of zero. As can be seen, the curves deviate significantly from linearity especially when the data of scattered intensity of aged sample are included. The semilogarithmic plot of $I(Q,t)$ versus $t$ may yield a very large error in the determination of relaxation rate $\Gamma$. Within the time scale of the experiments, $I(Q,\infty)$ values are not small enough to be negligible and the relaxation rate $\Gamma$ is $Q$ and time dependent. Since $I(Q,\infty)$ values cannot be estimated within the time scale of the experiment, we attempt to estimate relaxation rate $\Gamma$ by a following way.

Differentiation of the scattered intensity with respect to time, equation (5.26) can be written as

$$\frac{dI(Q,t)}{dt} = I(Q,\infty)\frac{d\alpha(t)}{dt} - 2\Gamma I(Q,0)\exp(-2\Gamma t)$$

$$= I(Q,\infty)\frac{d\alpha(t)}{dt} + (2\Gamma)I(Q,\infty)\alpha(t) - 2\Gamma I(Q,t)$$

$$= A(Q,t) - 2\Gamma I(Q,t) \quad (5.29)$$

With this equation, the $\Gamma$ can be evaluated from the slope of the plot of $dI(Q,t)/dt$ against $I(Q,t)$.

Figures (5.51) and (5.52) show representative plots of $dI/dt$ versus $t$ and $I(Q,t)$ at $Q$=0.028/Å$^{-1}$ and $Q$=0.048/Å$^{-1}$, respectively. Similar plots are obtained for other $Q$ values. The apparent diffusion coefficients are obtained from the slopes in the plots of $dI/dt$ versus $I$ and plotted as a function of $Q$, shown in figure (5.53). The values of $D$ are between $1.5\times10^{-13}$-$2\times10^{-14}$ cm$^2$/s in the $Q$ range of 0.017-0.072/Å$^{-1}$. The average value of $D$ around peak range (0.028-0.048/Å$^{-1}$) of aged sample is about $3.5\times10^{-14}$ cm$^2$/s. The $D$ value at the peak position of aged sample ($Q=0.032/Å^{-1}$) is about $3.8\times10^{-14}$ cm$^2$/s. The results show that at 46°C the apparent diffusion coefficient of aged 1:4 $C_{30}H_{62}/C_{36}D_{74}$ mixture may be very small and has a magnitude order of $10^{-14}$ cm$^2$/s.

As can be seen in figure (5.52), the results may include errors due to the absence of data between aged state and time scale of the experiments. Three estimated data are therefore
Figure(5.51) Plots of $\frac{dl}{dt}$ versus $t$ at $Q/\AA^{-1}$: 0.028 and 0.048.

Figure(5.52) Plots of $\frac{dl}{dt}$ versus $I(Q,t)$ at $Q/\AA^{-1}$: 0.028 and 0.048.

inserted between aged state and time scale of the experiments by adjusting a line in the plot of $\frac{dl}{dt}$ versus $t$. Figure(5.54) shows log-log plots of $I$ versus $t$. The plots of $\frac{dl}{dt}$ versus $t$ are displayed in figure(5.55). The plots of $\frac{dl}{dt}$ versus $I(Q,t)$ at different $Q$ are shown in figure(5.56). The empty circles in these figures are the inserted data.
Figure (5.53) The plot of the apparent diffusion coefficient as a function of Q. The error limit is 15%.

Figure (5.54) Log-log plots of I versus t at different Q. 1: 0.024/Å⁻¹, 2: 0.028/Å⁻¹, 3: 0.032/Å⁻¹, and 4: 0.040/Å⁻¹.

In figure (5.57), the plot of the apparent diffusion coefficient as a function of Q is shown. The Q² dependence of the rate is displayed in figure (5.58). The Q independence of the apparent diffusion coefficient is estimated from the slope of figure (5.58) to be $1.5 \times 10^{-14}$ cm²/s by a linear regression. If it is assumed that there is a Q⁴ term in $\Gamma$, the apparent diffusion coefficient is estimated to be $2 \times 10^{-14}$ cm²/s from a parabolic regression. The magnitude order of apparent diffusion coefficient obtained from long time ageing 1:4 mixture is consistent with experimental results in pure C₂0H₄₂[54] and calculations[55].
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Figure (5.55) Plots of $\frac{dl}{dt}$ versus $t$ at $Q/A^1$: 1: 0.028 and 2: 0.040.

Figure (5.56) Plots of $\frac{dl}{dt}$ versus $I(Q,t)$ at different $Q$: a: 0.028/Å⁻¹, b: 0.032/Å⁻¹, and c: 0.040/Å⁻¹.

This agreement indicates that the vacancy model proposed to account for self-diffusion in pure paraffins appears to be appropriate or, at least, is dominant for the dissolution of a well-separated two-phase mixture significantly unbalanced in concentration.
Chapter 5  Kinetics of The Demixing in Paraffin Mixtures

Figure (5.57) A plot of apparent diffusion coefficient as a function of Q. The error limit is ±15%.

Figure (5.58) A plot of rate as a function of $Q^2$. The error limit is ±15\%.

It should be pointed out that the effect of orientation fluctuation on SANS at smaller angles have been assumed to be small. Recent studies [56] of liquid crystal polymers have shown the effect of orientation fluctuation on SANS and light scattering (LS) are quite different. The order fluctuations in SANS at smaller angles are small and could be negligible. The case in LS is more complex, both concentration and order fluctuations play a significant role. Of course, the results are some restrictive since the order fluctuation does exist although small.
5.7 CONCLUSIONS

This Chapter primarily focuses on quantitative analysis of the concentration dependence and temperature dependence of kinetics of microphase separation in C30/C36 mixtures. The interpretation of the data has been done in terms of contemporary theories and phenomenological description. We also have quantitatively investigated microphase separation and the dissolution of microphase-separated domains in terms of the models. Conclusions drawn from these analyses are summarized below.

(1) Several dynamic scaling functions have been successfully tested, for the first time, for the molecular chain demixing mechanism in these highly crystalline and highly oriented solids involves the degree of conformational ordering and vacancies. Like other systems such as metal alloys and polymer blends, in this system also diffusion plays an essential role. The results indicate that the microphase separation in the present system obeys a universal process in which a system is initially unstable or metastable and starts to undergo a spontaneous ordering process, leading first to growth of small clusters of ordered domains, and later to coarsening of domains, and finally to approaching its uniformly ordered equilibrium state.

(2) It has also been found that ordering kinetics in C30/C36 mixtures follow a logarithmical growth law, and the exponent m (see text) depends on the temperature and concentration. The results seem to indicate that the vacancies and conformational disorder could have the same effect on the ordering kinetics as a diffusive impurity. We have suggested that the vacancies first provide transient paths for the migration of molecular chains and later hinder the demixing due to their accumulation in boundaries between lamellae. However, vacancies and conformational disorder as well as their mobility, accumulation, and trapping should be much more important for the demixing of short and stiff chain molecules than usually envisaged. The present work has raised more heuristic considerations, both theoretically and experimentally, in this respect.

(3) The results indicate that in the concentration range investigated, the time required for samples more unbalanced in concentration of the two components to reach an equilibrium is shorter than that for samples less unbalanced in concentration. Furthermore, between room temperature and 45°C, the time required for samples to reach an equilibrium is
shorter the closer the sample is in temperature to 45°C.

(4) The rate of microphase separation and the resultant equilibrium morphology are both significantly influenced by the isotope effect. At the same temperature, the time required for the D/H pair to reach an equilibrium is shorter than that for the H/D pair. The domains of $C_{36}H_{74}$ tend to stack above one another during microphase separation, which causes more unsymmetry in domain size for $C_{30}D_{62}/C_{36}H_{74}$.

(5) The kinetics of microphase separation can be described by Cahn's model. The kinetic of two phase dissolution in long time aged sample can be described by Summerfield-Ullman model.
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5.8 REFERENCES


2. aR.G. Snyder, M.C. Goh, V.J.P. Srivatsavoy, and H.L.Strauss, J. Phys. Chem. 96, 10008 (1992), therein references


Chapter 5 Kinetics of The Demixing in Paraffin Mixtures

44. J. W. Christian, The theory of Transformation in Metals and Alloys, Part 1:
    Equilibrium and General Kinetic Theory, Pergamon, New York, 1981
    Rev. Lett. 64, 2285 (1990)
46. M. Avrami, J. Chem. Phy. 7, 1103 (1939); 8, 212 (1940); 9, 177 (1941)
48. P. de Gennes, Scaling Concepts in Polymer Physics, Cornell University Press,
    Ithaca, NY, 1979
    1986
Chapter 5  Kinetics of The Demixing in Paraffin Mixtures

56. A. Ten Bosch, J. Phys. II France 1, 949 (1991) therein references
CHAPTER SIX STUDIES OF AGGREGATION IN MIXTURES OF PARAFFIN AND POLYDIMETHYLSILOXANE

6.1 INTRODUCTION

Studies are extended to aggregation phenomena in mixtures of paraffins and polymers. The experimental results are related to current theories.

Aggregation in polymer systems is a very common phenomenon observed in various experimental situations such as, for instance, polymers in their poor solvents, copolymers, polymer ionomers, microemulsions, and colloidal polymer systems. The reasons for the aggregation are complex and should be individually discussed for different systems. The interpretation of scattering patterns from aggregating systems, on the other hand, are usually based on models which reflect inner structures of the aggregate. In this chapter, the aggregation in mixtures composed of paraffins and polydimethylsiloxane (PDMS) is investigated by using small angle x-ray scattering (SAXS). Various models and forms for the correlation function, the Fourier transform of which gives the scattering, are considered; theoretical and measured scattered intensities are compared. We primarily report here an effort to model the aggregation behavior and the structure of paraffin/PDMS mixtures by proposing a new correlation function.

The phase diagrams of mixtures of the oligomer PDMS mixed with paraffins (or oligomer polyethylene) and thermodynamics of mixtures have been reported by Huglin et al.[1-3]. The types of phase diagram observed are shown in figure (6.1). Type I is for the liquid paraffins mixed with PDMS irrespective of the molecular weight of PDMS, this phase diagram is temperature insensitive; type II is for mixtures in which only one of the components is of large molecular weight, and if the molecular weight of PDMS is higher (but still in the molecular weight range of oligomer), the phase diagram may show the type III behavior. In the present aggregation study, the mixtures are composed of liquid paraffins and high molecular weight PDMS rather than oligomer. They may qualitatively belong to the type I phase diagram class.
Chapter 6 Studies of Aggregation in Mixtures

Figure 6.1 General forms of phase diagrams observed for mixtures of oligomer PDMS and paraffins [see references 1-3].

The chapter is arranged as follows. In the second and third parts, the experiment and preliminary data reduction are described. In the fourth and fifth parts, the existing models are evaluated and the experimental scattering patterns are fitted by them. Then, a new correlation function is proposed and used to model the experimental data. In the seventh part, the fractal dimension of mixtures is determined by using the power-law. Finally, the conclusion is given in the eighth part.

6.2 EXPERIMENTAL DETAILS

Liquid mixtures of paraffins (Aldrich) and polydimethylsiloxane (PDMS) (Aldrich) were used in the investigation of the aggregation behavior. For PDMS, the characterization data given are weight-average molecular weight $M_w = 93,700$ and polydispersity index of molecular weight $d = 3$ obtained by gel permeation chromatography (GPC). $C_{12}H_{26}$, $C_{16}H_{34}$, and $C_{18}H_{38}$ have high purity (99%). In order to remove possible cyclic PDMS species, the samples were washed several times with acetone at room temperature since the cyclic
species are much more soluble in acetone than the linear. Weighed amounts of paraffins and PDMS were mixed and heated at 150°C in a nitrogen atmosphere for at least 4 hours and then at 100°C for several hours. The mixtures were specified as weight percent of PDMS. For the samples with less PDMS, the turbidity was found in several days after the samples were made.

The details about SAXS measurements have been given in Chapter 2. The samples were injected into a sample holder which was heated by means of circulating water. The thermocouple was placed as close as possible to the samples. The temperature was held constant at ± 0.3°C. The samples were kept at measured temperatures at least one hour before SAXS measurements.

6.3 PRELIMINARY DATA REDUCTION

As discussed in Chapter 2, the background scattered intensity resulting from thermal density fluctuations should be subtracted from the observed x-ray scattered intensity I(Q). Otherwise, interpretations of data obtained from higher Q would become confused and even impossible. Thermal density fluctuations usually contribute to the scattering at higher Q for small angle x-ray scattering. The elimination of this scattering for pinhole collimation has been discussed in Chapter 2.

![Figure(6.2)](image)

**Figure(6.2)** The plot of IQ^4 versus Q^4 of SAXS data obtained from the PDMS/C_{16}H_{38} liquid mixture (45% PDMS) at 30°C. The slope of least-squares fit of the data at higher Q produces a amount of the thermal density intensity to be subtracted.
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Figure (6.3) SAXS profiles obtained from the PDMS/C$_{16}$H$_{34}$ liquid mixture (45% PDMS) at 30°C before (filled circle) and after (open circle) background correction.

A typical plot of IQ$^4$ versus Q$^4$ is illustrated in figure (6.2). The representative scattering patterns before and after thermal fluctuation background correction are shown in figure (6.3). The elimination has been carefully done in order to avoid overcorrections.

6.4 BASIC FORMULAE AND EXISTING MODELS

The small angle X-ray scattering from a system is proportional to the Fourier transform of the electron density correlation function $\gamma(r)$ [4-6], given by

$$
\gamma(r) = \frac{\int \eta(r) \eta(r + r') dr}{\sqrt{V} \langle \eta^2 \rangle}
$$

(6.1)

where the integration is over the illuminated volume $V$, $\eta(r)$ is the fluctuation of the electron density at $r$ and $\langle \eta^2 \rangle$ indicates an average over $V$. For a homogeneous phase system, which is known to be certain problems, $\gamma(r)$ contains information about surface areas which can be measured by using small angle x-ray scattering. However, for a heterogeneous system, for example, a phase separated or aggregated system, it is not possible to characterize the systems directly from the scattered intensity without a model for the electron density distribution. The correlation function $\gamma(r)$, reflecting the physically realistic and practical framework, therefore plays a very important role in these systems. When a correlation function $\gamma(r)$ is known, one can calculate the scattered intensity as a function of wavevector, compared with experimental scattered intensity, and
then can obtain information about characteristics of systems.

For a spatially isotropic system, the correlation function is a function only of the magnitude \( r \), and the scattered intensity can be expressed as

\[
I(Q) = \langle \eta^2 \rangle \int \frac{\sin(Qr)}{Qr} 4\pi r^2 \, dr
\]  
(6.2)

\( \gamma(r) \) and \( \langle \eta^2 \rangle \) may be determined from the Fourier inversion of the scattered intensity by

\[
\gamma(r) = \int I(Q) \frac{\sin(Qr)}{Qr} Q^2 dQ / \int I(Q)Q^2 dQ
\]  
(6.3)

and

\[
\langle \eta^2 \rangle = 4\pi \int I(Q)Q^2 dQ
\]  
(6.4)

Before a new model is proposed, existing correlation functions are summarized as follows. For a spatially isotropic but heterogeneous system, the correlation function, for the simplest case, can be given by an exponential form as proposed by Debye and co-workers[6],

\[
\gamma(r) = \exp(-r/a_0)
\]  
(6.5)

where the quantity \( a_0 \) usually represents a correlation distance defining the size of heterogeneities. This form is obtained by considering the so-called stick probability \( P_{ij} \) which is the probability that a stick of length \( r \), placed at random in the system, will have one end in phase \( i \) and another end in phase \( j \). The quantity \( dP_{ij}/dr \) differs from zero according to this probability, so that extending \( r \) to \( r+dr \) leads to a crossing from one phase to another. Substituting equation (6.5) into equation (6.2), we have[8]

\[
I(Q) = \frac{8\pi \langle \eta^2 \rangle}{a_0^3} \frac{a_0^3}{1 + a_0^3 Q^2}
\]  
(6.6)

Equation (6.6) can be used for heterogeneous systems in which the interfaces of domains are sharp. The scattering is to be proportional to \( Q^{-4} \) in the limit of large \( Q \), i.e., Porod’s law. According to Debye et al[6], another static parameter, the correlation distance \( L_c \), can be described in terms of a single exponential correlation function \( \gamma(r) \).

\[
L_c = \int_0^\infty \gamma(r) \, dr = a_0
\]  
(6.7)
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It is often appropriate to express the data by a summation of short- and long-range terms represented by two exponential terms

\[
\gamma(r) = f \exp(-r/a) + (1-f)\exp(-r/a_0)
\](6.8)

or an exponential and a Gaussian term[9]

\[
\gamma(r) = f \exp(-r/a) + (1-f)\exp(-r^2/a_0^2)
\](6.9)

where the fraction factor, \(f\), weights the contribution of the exponential short-range term.

These two correlation functions involve four parameters, they are computationally easy but without theoretical justification.

For systems composed of ordered particles or lamellar domains with random orientation, or highly interconnected structures, the scattering profile usually shows a peak. In these cases, the exponential form of the correlation functions are not able to describe the scattering patterns. Ciccarello[10] first proposed to modify the exponential form in two ways:

(1) exponential-sine correlation function

\[
\gamma(r) = \exp(-r/a_0)\sin(br)/(br)
\](6.10)

(2) exponential-cosine correlation function

\[
\gamma(r) = \exp(-r/a_0)\cos(br)
\](6.11)

These correlation functions can be Fourier transformed to give scattered intensity analytically. Substituting exponential-sine and exponential-cosine correlation functions into equation(6.2), integration gives

\[
I(Q) = 8\pi < n^2 > a_0 \frac{8\pi < n^2 > a_0^3}{[1 + a_0^2(Q - b)^2][1 + a_0^2(Q + b)^2]}
\]

and[11]

\[
I(Q) = 4\pi < n^2 > a_0 \frac{1 + b/Q}{[1 + a_0^2(Q + b)^2]^2} + \frac{1 - b/Q}{[1 + a_0^2(Q - b)^2]^2}
\](6.12)

Again, the characteristic \(Q^{-4}\) dependence of the intensity distribution at larger wavevectors is observed for an exponential-sine and an exponential-cosine correlation functions. Teubner and Strey[12] brought the structural and thermodynamic viewpoints together by using an order parameter expansion of the phenomenological Laudau free energy function. Considering the change in free energy as fluctuations of the order parameter,
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they arrive at the exponential-sine correlation function, \( \gamma(r) = \exp(-r/a_0) \sin(2\pi r/d)/(2\pi/d) \)
and scattering function given by

\[
I(Q) = \frac{8\pi/a_0 \langle \eta^2 \rangle}{a_2 + c_1 Q^2 + c_2 Q^4}
\]

where \( d \) is also characteristic for the domain size with a period, \( a_2, c_1, \) and \( c_2 \) are order parameters in the following phenomenological Laudau free energy \( F \)

\[
F = \int [a_2 \eta^2 + c_1 (V\eta)^2 + c_2 (\Delta\eta)^2] \, d^3r
\]

and the relationships between ordered and static parameters are given by

\[
a_0 = \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{1/2} + \frac{1}{4} \frac{c_1}{c_2} \right]^{-1/2}
\]

and

\[
d = 2\pi \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{1/2} - \frac{1}{4} \frac{c_1}{c_2} \right]^{-1/2}
\]

SANS and SAXS profiles obtained from microemulsion systems were fitted very well by equation(6.14). Similarly, Wang et al [11] used the exponential-cosine correlation function to describe the phase separation in a polymer blend. They too are able to fit light scattering curves well.

Correlation distances \( L_c \) corresponding to exponential-sine and exponential-cosine correlation functions are given in terms of equation(6.7), respectively.

\[
L_c = \frac{1}{b} \arctan\left( \frac{1}{a_0 b} \right)
\]

and

\[
L_c = \frac{a_0}{1 + a_0 b^2}
\]

Vonk et al[13] presented another model based on a disordered lamellar structure. The one dimensional correlation function was given by a composition-dependent linearly periodic function. The three dimensional correlation function for the distortion structure they arrived at is identical to those in equations (6.10) and (6.11) except that trigonometric functions are replaced by a three dimensional function of ideal structure. This correlation function can also describe systems with partially ordered structures, and therefore can predict the scattering patterns displaying a maximum.
A few comments concerning the fitting of the experimental scattering data with the multiparameter models should be made. The fitting was initially done without resorting to a least-squares fitting procedure using the following protocol. The initial value of the parameter $a_0$ is estimated by a plot of $I^{-0.5}$ versus $Q^2$, the Debye-Bueche plot. The initial choice of the parameter $b$ is determined by the location of a peak in a scattering pattern. With the overall shape of the scattering pattern fit, the predicted scattering curve can be scaled to the scattered intensity found experimentally with the constant $K$. Then, the best parameters are determined by a least-squares method. This protocol was used in determining the parameters of equation (6.13) [11]. Alternatively, equation (6.14) can be rewritten as a polynomial: $1/I(Q)=A_0+A_2 Q^2+A_4 Q^4$, and the parameters $a_0$ and $d$ are determined by the following equations: $a_0=[(A_0/A_4)^{0.5}/2+(A_2/A_4)/4]^{-0.5}$ and $d=2\pi[(A_0/A_4)^{0.5}/2-(A_2/A_4)/4]^{-0.5}$. It should be pointed out that the scattering distribution yields a single peak provided $A_0>0$, $A_2<0$, and $A_4>0$ [12].

6.5 FITTING SCATTERING PATTERNS WITH EXISTING MODELS

In previous section, existing models have been evaluated. Since the small angle x-ray patterns obtained from paraffin/PDMS liquid mixtures show a peak, the Debye and other exponential correlation functions have to be ruled out immediately. Exponential-sine and exponential-cosine correlation functions, as discussed above, can describe the statistical features of isotropic but heterogeneous systems with partially ordered structures. The corresponding scattered intensity formulae can predict a scattering pattern with a peak. In this section, through comparison of model calculations with the experimental data obtained from $C_{16}H_{34}/PDMS$ liquid mixtures, the structure is examined. As is known, characteristic $Q^{-4}$ dependence of scattered intensity distribution at large wavevectors is related to a structure which differs from one without this dependence. In the comparisons of the existing models with the experimental data, the most important feature is to see whether Porod's law that is predicted by existing models is expected or not. Figure (6.4) shows SAXS patterns (open circle) obtained from PDMS/$C_{16}H_{34}$ liquid mixture with 45% PDMS at different temperatures. The calculated scattered intensities in terms of an exponential-sine correlation function were given in solid lines by using a nonlinear least-squares method. As seen in the figure, application of the exponential-sine correlation...
Figure 6.1: Scattering patterns of the YDMPC/PCP system heated to (a) 30°C, (b) 40°C, (c) 50°C, and (d) 60°C, and (e) 70°C for different temperatures, as shown in the figure. The data points are shown as circles, and the best fit to the data is shown as a solid line. The X-axis represents the scattering vector (Q), and the Y-axis represents the intensity (I). The graphs show the expected behavior of the system as the temperature is increased.
Figure (6.4) Scattering patterns of the PDMS/C_{16}H_{34} (45\% PDMS) liquid mixture at:
(a) 30°C, (b) 40°C, (c) 50°C, (d) 60°C, and (e) 78°C. Solid lines were obtained by equation (6.12).

function is not able to fit the patterns. In particular, the calculated data significantly deviate from experimental ones over a wide range and follow Porod’s law at larger Q. A typical log-log plot of the calculated scattering pattern with exponential- sine correlation function is shown in figure (6.5), which indeed gives Porod’s law at larger Q. It is noteworthy that the range where calculated data begin to deviate significantly from experimental data is at a lower Q than the usual Porod’s region. Even disregarding the peak and fitting data only at fairly large Q, an improved fit in this region could not be obtained. Some deviations between experimental and calculated data around peak were also observed. Similar deviations at smaller Q were found in the fits for microemulsion systems with the same correlation function[12].

Figure (6.5) A Log-log plot of the calculated intensity versus wavevector with equations (6.14), (6.16), and (6.17) for the PDMS/C_{16}H_{34} (45\% PDMS) liquid mixture at 40°C. \(a_0=41\text{Å}, d=140\text{Å}\).
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Figure (6.6) Scattering patterns of the PDMS/C_{16}H_{34} (45% PDMS) liquid mixture at different temperatures: (a) 30°C, (b) 40°C, (c) 50°C, (d) 60°C, and (e) 78°C. Solid lines were obtained by equation (6.13).

Application of an exponential-cosine correlation function to the same experimental data is shown in figure (6.6). A similar curve-fitting procedure was followed. In this case, the data at smaller wavevectors are fitted well, but data in the high Q range still show deviations although this model generally looks appreciably better than the exponential-sine model, especially at smaller Q. The calculated scattered intensities, as expected, also decay in the form of Porod's law at larger wavevectors, as shown in figure (6.7).

Figure (6.7) A Log-log plot of the calculated intensity versus wavevector with equation (6.13) for the PDMS/C_{16}H_{34} liquid mixture (45% PDMS) at 40°C. a_0=22\,\text{Å}, b=0.024\,\text{Å}^{-1}.

The above calculations clearly indicate that the exponential-sine and the exponential-cosine correlation functions have the characteristic Q^{-4} dependence of scattered intensity distribution at large wavevectors and are not applicable to our data. Actually, if it is supposed that the scattered intensity be simply proportional to Q^d, power-law, plot of
logI versus logQ from the experimental data of PDMS/C$_{16}$H$_{34}$ liquid mixture with 45% weight fraction of PDMS at 40°C produces a slope of about -1.7 rather than -4, as shown in figure (6.8). This is significantly different from Porod's law and therefore cannot be described by the models. Full curve-fitting, including peak and curve tail, of course, may not give a simple relationship. Because the deviation from Porod's law may not simply be a parametric problem but may reflect the nature of structural differences, it is necessary that we should reconsider this problem carefully. This problem will be dealt with in the forthcoming section.

6.6 A NEW MODEL

In the preceding section, it has been found that the correlation functions discussed above cannot be fitted to scattering function in Porod's law region for the PDMS/C$_{16}$H$_{34}$ liquid mixtures. Recently, theoretical and experimental studies[19-23] have demonstrated that for systems with self-similar structures, the scattered intensity is not proportional to $Q^{-4}$ but $Q^{D_f}$, where $D_f$ is smaller than -4 and generally fractional. The fractal structures have been found in many systems as we previously mentioned. Because the parameter $D_f$ can control the variations of scattered intensity at larger wavevectors, a heuristic consideration is the fitting to the whole scattering pattern may be improved if the correlation function contains this feature. In this section, a new correlation function is proposed for this requirement.
Here we retained the exponential-cosine correlation function in equation (6.11) and, as discussed in fractal theories [19-23], introduce a fractal correlation function \( r^{D-D_f} \) to define a new correlation function in the form

\[
\gamma(r) = \frac{1}{r^{D-D_f}} \exp(-r/a_0) \cos(br)
\]

(6.20)

where \( a_0 \) and \( b \) have the same physical meanings discussed above, \( D \) and \( D_f \) are the space and fractal dimensions, respectively. The shapes of fractal correlation function and its combinations with other parts in equation (6.20) are schematically illustrated in figure (6.9). Physically, this new correlation function has clear meaning. For a really physical fractal system, as opposed to a mathematical system, the scale invariance in the system is finite and limited between \( r_{\text{max}} \) (finite size of clusters or domains) and \( r_{\text{min}} \) (finite size of particles making up the clusters or domains). Mathematically, the lower cutoff point must be convergent. The simplest correction for equation (6.20) is to set \( \gamma(r) \) to zero for \( 0 < r < 2r_0 \), where \( 2r_0 \) is the particle radius, \( R_g \) is radius of gyration, which means the particle centers can not approach closer than \( 2r_0 \). The Debye correlation function \( \exp(-r/a_0) \) here, as discussed in the literature [16,18], can be considered as a scaling function characterized by a single effective cutoff length \( a_0 \) (correlation distance) for systems where the aggregates have a finite size and may be quite entangled. This scaling function represents the probability that the fractal correlations around a given particle exist for distances greater than or equal to \( r \). It should be pointed out that since there are some deficiencies in the form of the fractal function, as discussed by Martin and Hurd [14], here we suggest the meaning of parameter \( D_f \) be explained with care although it has been termed a fractal dimension and has been used herein. We prefer to consider \( D_f \) as a parameter controlling variations of the scattered intensity at larger wavevectors, and equation (6.20) is a modification of Debye’s correlation function. In three dimensions, by putting \( D_f = 3 \), the equation (6.20) is simplified to the exponential-cosine form, and further by putting \( b = 0 \), the model is reduced to a completely random model, e.g. the Debye model. By proceeding cautiously in this way we also underline the problem of the best values in such multiparameter fits.

For exponential-sine and exponential-cosine correlation functions, negative values of the functions are sometimes obtained. This has been explained as very low probabilities of
Figure (6.9) Correlation functions $\gamma(r)$: (a) infinite cluster, (b) cluster with upper cutoff at $r = a_0$, (c) cluster with both upper and lower cutoff [see ref.15], and (d) equation (6.20).
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Figure (6.10) The intensity distribution given by equation (6.21) in solid line. Dashed and line-dotted lines represent contributions of the first and second terms in equation (6.21).

Figure (6.11) Influences of parameter \( D_f \) on the shape of scattered intensity distribution at fixed \( a_0 \) and \( b \) in equation (6.21).

Finding scatterers within these distances and has a similar physical meaning to the concept of excluded volume [11]. The average size of clusters or domains is equal to \( 2\pi/b \).

Substituting equation (6.20) into equation (6.2) and carrying out Fourier transform, we have

\[
I(Q) = \frac{2\pi a_0^0}{a_0 Q} \left[ \frac{\sin((D_f - 1)\arctan((Q + b)a_0))[1 + (Q + b)^2 a_0^2]^{1/2}}{[1 + (Q + b)^2 a_0^2]^{n/2}} \right] + \frac{\sin((D_f - 1)\arctan((Q - b)a_0))[1 + (Q - b)^2 a_0^2]^{1/2}}{[1 + (Q - b)^2 a_0^2]^{n/2}} \Gamma(D_f - 1)
\]

(6.21)

where \( \Gamma \) is a gamma function. Unlike the structure factor in the expression derived by Frendo, Kjems, and Sinha (FKS) [18], equation (6.21) is made up of two terms which differ.
from each other only in the sign in the front of parameter $b$. It can be seen that the structure factor in the FKS expression would be a special case of equation (6.21). For $b=0$, equation (6.21) can be reduced to the structure factor in the FKS expression. In the cases of $b=0$ and $a_0Q\gg 1$, $I(Q)$ is proportional to $Q^{D_f}$, as expected from the fractal nature of the correlations between the particles. Note that in equation (6.21) both $a_0(Q+b)\gg 1$ and $a_0(Q-b)\gg 1$ requires parameter $b$ be very small and $a_0$ be large, which, in view of fractal theory, may indicate no simple power law existing for a fractal system with smaller average size of clusters or domains and with partial ordering. The scattered intensity calculated from equation (6.21) as a function of wavevector is shown in figure (6.10) by a solid line. The dashed and line-dotted lines in this figure represent the contributions of the first and second terms in the equation (6.21). The influences of parameters $a_0$ and $b$ on the curve have been discussed. The influence of parameter $D_f$ on the curve is schematically shown in figure (6.11). It is found that $D_f$ influences the entire curve: the curve tail is up at larger angles and the peak becomes broader at smaller angles as $D_f$ decreases.

Because equation (6.20) has a lower cutoff at small $r$, equation (6.21) may not properly describe scattered intensity in the range of $0<r<r_0$. In order to have mathematical meaning for the lower cutoff, equation (6.20) has been set to be zero for $0<r<2r_0$. In this case, $I(Q)$ can still be written in the following form

$$I(Q) = \frac{2\pi a_0^{D_f}}{a_0Q} \left\{ \frac{(D_f - 1)[1 + (Q + b)^2 a_0^2]^{1/2}}{[1 + (Q + b)^2 a_0^2]^{D_f/2}} \text{Im}\{\Gamma(D_f - 1,(2r_0/a_0)(1 - i(Q + b)a_0))\} + \frac{(D_f - 1)[1 + (Q - b)^2 a_0^2]^{1/2}}{[1 + (Q - b)^2 a_0^2]^{D_f/2}} \text{Im}\{\Gamma(D_f - 1,(2r_0/a_0)(1 - i(Q - b)a_0))\} \right\}$$

where $\Gamma(\alpha, \beta)$ is the incomplete gamma function with complex argument defined by the complex integral

$$\Gamma(\alpha, \beta) = \int_{\beta}^{\infty} w^{\alpha-1} \exp(-w) \, dw$$

(6.22)
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For $Qr_0 \leq 1$, equation (6.22) will be reduced to equation (6.21). The experimental data in terms of the adjustable parameters $a_0$, $b$, $D_f$, and $r_0$ can be fitted by using the two models (6.21) and (6.22). The calculations will show that present experimental data are not sensitive to the difference between the two forms. Equation (6.21) is therefore used to fit experimental data. The fitting process is the same as in the previous discussion.

The correlation distance $L_c$ corresponding to equation (6.20) can be determined in terms of equation (6.7). The parameters $a_0$ and $b$ calculated from different correlation functions can be quite different but parameter $L_c$ may be on the same order if different correlation functions can be used to describe the same system.

### 6.7 FITTING SCATTERING PATTERNS WITH THE NEW MODEL

The experimental data obtained from PDMS/C$_{16}$H$_{34}$ liquid mixture at different temperatures were fitted by equation (6.21). The calculated data produce the solid lines shown in figure (6.12). As can be seen from this figure, scattering patterns are fitted very well up to high $Q$ by using the correlation function proposed in this work. The parameters obtained are summarized in table 6.1. The results show that correlation distances slightly decrease with increasing temperature. The value of $D_f$ obtained is the same as, or close to, the one reported in the literature. Studies on compacted vapor-phase aggregates of silica using small angle neutron scattering by Sinha, Freltoft, and Kjems (SFK)[16] gave the $D_f$ value of 2.52. The measurements of SANS were extended to compressed powders of aggregates of fine silica particles and gave the $D_f$ value of 2.61[18]. The early stage of the aggregate formation in Cab-O-Sil measured by light scattering gave the $D_f$ value of about 2.5[19]. These values are close to the value of the diffusion-limited aggregation model of Witten and Sander[20] in their computer simulations. These values are not agreement with the $D_f$ value of 1.88 obtained from the light- and x-ray scattering measurements on fumed silica dispersed in dilute solution by Martin, Schaefer, and Hurd with power-law[21]. As can be seen in table 6.1, the value of $D_f$ appears to be independent of the temperature, i.e. independent of the macroscopic
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Figure 6.12: Scattering functions for the rotary diffusion of different temperatures. The solid and dashed lines were obtained by fitting the theoretical point $D_{10}$ to the rotational mean square displacement distribution and other statistical parameters. The parameter $D_{10}$ decreases with increasing temperature. In each graph, the frictional coefficient is smaller, as shown by the peak parameter $D_{10}$ should be a measure of the size of the distribution. The correlation function $C(t)$ is also shown.

TABLE 6.1: The parameters obtained from the Frisch method for the function $C(t)$. The results are shown in the table below.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$D_{10}$</th>
<th>$D_{11}$</th>
<th>$D_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>T2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>T3</td>
<td>0.1</td>
<td>0.05</td>
<td>0.01</td>
</tr>
</tbody>
</table>

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density, which is also in agreement with the results obtained by Sinha, Freltoft, and Kjems[18]. However, if the parameter $D_f$ is considered to be a fractal dimension, the temperature independence of $D_f$ is really a confused result, which is in disagreement with other statistical parameters and the fractal theory [22]. As can also be seen in table 6.1, the parameter $a_0$ decreases with increasing temperature, indicating less aggregation at higher temperature. In view of the fractal theory[22], if the structures take on a sparser appearance, the fractal dimension is smaller, as shown in figure(6.14), which implies the parameter $D_f$ should decrease with increasing temperature if it really was a measurement of the dimension. It seems that the correlation function adopted in the form of

$$\text{equation (6.20)}$$

will give a larger value of $D_f$, probably around 2.6, than that obtained from the log-log plot of scattered intensity versus wavevector. In view of fractal theories, the exponential form as a scaling function is too simple. The more complicated forms of scaling function should be considered as has been done by Aharony[23]. Considering modifications of Debye’s random correlation function, the scattered intensity distribution

**TABLE 6.1** The parameters obtained from equation (6.21) by using the least-squares method for the PDMS/C$_{16}$H$_{34}$ (45% PDMS) liquid mixture at different temperatures

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>78</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (±5)(Å)</td>
<td>74</td>
<td>70</td>
<td>65</td>
<td>63</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>$b$ (±0.003)(1/Å)</td>
<td>0.024</td>
<td>0.026</td>
<td>0.026</td>
<td>0.027</td>
<td>0.028</td>
<td>0.029</td>
</tr>
<tr>
<td>$D_f$ (±0.2)</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>$L_c$ (±0.5)(Å)</td>
<td>10.5</td>
<td>10.0</td>
<td>9.8</td>
<td>9.6</td>
<td>9.4</td>
<td>9.2</td>
</tr>
</tbody>
</table>

...
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Figure (6.13) Calculated correlation functions in terms of equation (6.20) for the PDMS/C$_{16}$H$_{34}$ liquid mixture (45% PDMS) at different temperatures by using parameters in Table 6.1. Temperatures are (a) 30°C, (b) 50°C, (c) 60°C, and (d) 78°C. Arrows indicate the average sizes of aggregates.
has been fitted very well in the whole range of the wavevector due to the introduction of parameter $D_f$. Although our results are in excellent agreement with those reported theoretically and experimentally, and may contain the nature of the fractal behavior as discussed by Sinha, Freltoft, and Kjems (SFK)\[16], we prefer to consider $D_f$ as a parameter controlling the variations of the scattered intensity at a wavevector range.

In figure(6.13), the new correlation functions corresponding to figure(6.12) are presented by using the parameters listed in table 6.1. The shape of the curve has a feature commonly seen in other correlation functions. As the distance $r$ increases, the correlation function rapidly approaches zero, implying a loss of long range order due to the partial disorder in the structure. The positions of the first maxima in the curves correspond to the average sizes of aggregates. The average sizes of aggregates obtained from the two methods are given in table 6.2. Note that average sizes of aggregates obtained from equation(6.21) are slightly different to those obtained from the figure(6.13), which is because the value of the quantity $b$ is not exactly equal to the position of the peak. Considering a little deviation from peak position may cause a larger variation in the average size, this value obtained from the correlation function is preferred although both values are within the statistical error.

TABLE 6.2 The average sizes of PDMS$C_{16}H_{34}$ liquid mixture (45% PDMS)

<table>
<thead>
<tr>
<th>$T(°C)$</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>78</th>
</tr>
</thead>
<tbody>
<tr>
<td>size(±5)(Å)(eq.21)</td>
<td>260</td>
<td>240</td>
<td>240</td>
<td>230</td>
<td>220</td>
<td>220</td>
</tr>
<tr>
<td>size(±3)(Å)(fig.13)</td>
<td>240</td>
<td>220</td>
<td>220</td>
<td>210</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>
Figure 6.15 shows results obtained from different concentrations of PDMS/C\textsubscript{16}H\textsubscript{34} liquid mixture at 30°C. The scattered patterns are also perfectly reproduced by equation (6.21). The parameters obtained are listed in table 6.3. The calculated correlation functions in terms of table 6.4 are shown in figure 6.16. The correlation distances as functions of the PDMS composition are displayed in figure 6.17. As can be seen from these results, the
correlation distances decrease with increasing PDMS composition, which indicates the degree of heterogeneity in the system slightly decreases with increasing PDMS concentration. This result is supported by the scattered intensity patterns which show scattered intensity becomes slightly larger and the peak becomes sharper as the PDMS

Figure (6.16) Calculated correlation functions in terms of equation (6.20) for different concentrations of the PDMS/C₁₆H₃₄ liquid mixture at 30°C by using parameters in table 6.3. Concentrations of PDMS (by weight) (a) 30%, (b) 40%, and (c) 50%. Arrows indicate average sizes of aggregates.
content decreases. All results may be also qualitatively comparable to the type I phase diagram of liquid paraffins mixed with PDMS[1-3], indicating a slight temperature dependence. It is noted that, generally speaking, the parameter $D_f$ appears to be independent of concentration except for 50%. The value of $D_f=2.3$ was also observed for the same concentration at 60°C. This value may be due to less aggregation in the structure.

![Figure](image)

Figure(6.17) Correlation distances as function of composition of the PDMS /$C_{16}H_{34}$ liquid mixture at 30°C.

**TABLE 6.3 The parameters for PDMS /$C_{16}H_{34}$ liquid mixture at 30°C**

<table>
<thead>
<tr>
<th>PDMS(%)</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (±5)(Å)</td>
<td>85</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>$b$ (±0.003)(Å)</td>
<td>0.0148</td>
<td>0.0175</td>
<td>0.0275</td>
</tr>
<tr>
<td>$L_c$ (±0.5)(Å)</td>
<td>15.5</td>
<td>13.7</td>
<td>8.0</td>
</tr>
<tr>
<td>$D_f$ (±0.2)</td>
<td>2.65</td>
<td>2.65</td>
<td>2.30</td>
</tr>
<tr>
<td>Size(±5)(Å)</td>
<td>420</td>
<td>360</td>
<td>230</td>
</tr>
</tbody>
</table>

According to the fractal theory[17], as the fractal dimension decreases, the structures take on a sparser appearance, which seems to correspond to the lower degree of heterogeneity at this concentration. The influence of heterogeneity on the parameter $D_f$ should be examined further.

Scattering patterns of the same mixture with concentrations less than 30% were also obtained. The representative curves are shown in figure(6.18). The information in the experimental scattering curves is greatly reduced because the maximum in the first order peak is not resolved or pronounced. By inserting $b=0$, equation(6.20) is reduced to the
FKS expression. These curves can still be fitted reasonably well by the reduced form. But, consider that there may be a peak, we feel that the present procedure can not be applied in a meaningful way to these concentrations.

The $D_f$ value was found to be 2.4, and size independent of the different concentrations in the PDMS/C_{16}H_{34} liquid mixture. However, in the PDMS/C_{12}H_{26} liquid mixture is now considered. In this system there should be less degree of heterogeneity due to the shorter chain length. What we want to know is whether a peak appears in the scattering pattern and the value of the parameter $D_f$. For the similar concentrations, if there is a peak in scattering pattern of PDMS/C_{12}H_{26} liquid mixture, there should also be a peak in scattering pattern of PDMS/C_{16}H_{34} liquid mixture although the peak may not be resolved. For the system with less heterogeneity, the determination of the parameter $D_f$ could reveal the influence of the heterogeneity on the parameter.

Figure 6.18 Scattering patterns of the PDMS/C_{16}H_{34} liquid mixture at 40°C: (a) 5.5% PDMS and (b) 10% PDMS.

The PDMS/C_{12}H_{26} liquid mixture is now considered. In this system there should be less degree of heterogeneity due to the shorter chain length. What we want to know is whether a peak appears in the scattering pattern and the value of the parameter $D_f$. For the similar concentrations, if there is a peak in scattering pattern of PDMS/C_{12}H_{26} liquid mixture, there should also be a peak in scattering pattern of PDMS/C_{16}H_{34} liquid mixture although the peak may not be resolved. For the system with less heterogeneity, the determination of the parameter $D_f$ could reveal the influence of the heterogeneity on the parameter.
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Figures (6.19) and (6.20) show the fitting results and corresponding correlation functions for a PDMS/C_{12}H_{26} liquid mixture. The statistical parameters obtained are listed in table 6.4. The scattering patterns of this mixture at 22°C and 35°C were found to be the same. The D_f value was found to be 2.4, and also independent of the temperature, as it was for the PDMS/C_{12}H_{26} liquid mixture. The results indicate that the parameter D_f tends to

\[ D_f \approx 3 \]

TABLE 6.4 The parameters of PDMS /C_{12}H_{26} liquid mixture (19%)

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>a_0(±5)(Å)</th>
<th>b(±0.003)(1/Å)</th>
<th>D_f(±0.2)</th>
<th>L_c(±0.5)(Å)</th>
<th>size(±5)(eq21)(Å)</th>
<th>size(±3)(fig20)(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>70</td>
<td>0.025</td>
<td>2.4</td>
<td>11</td>
<td>250</td>
<td>240</td>
</tr>
<tr>
<td>29</td>
<td>70</td>
<td>0.025</td>
<td>2.4</td>
<td>11</td>
<td>250</td>
<td>240</td>
</tr>
<tr>
<td>35</td>
<td>70</td>
<td>0.025</td>
<td>2.4</td>
<td>11</td>
<td>250</td>
<td>240</td>
</tr>
</tbody>
</table>

Figure (6.19) Scattering patterns of the PDMS/C_{12}H_{26} liquid mixture (19% PDMS) at different temperatures: (a) 22°C and (b) 35°C. Solid lines were obtained by equation (6.21)
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Figure (6.20) Calculated correlation function in terms of equation (6.20) for the PDMS/C\textsubscript{12}H\textsubscript{26} liquid mixture (19\% PDMS) in the range from 22°C to 35°C by using parameters in table 6.4. Arrow indicates the average size of aggregates.

TABLE 6.5 The parameters for PDMS/C\textsubscript{18}H\textsubscript{38} liquid mixture (45\%)

<table>
<thead>
<tr>
<th>(T(°C))</th>
<th>40</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_0(±5)(Å))</td>
<td>85</td>
<td>70</td>
<td>65</td>
</tr>
<tr>
<td>(b(±0.003)(1/Å))</td>
<td>0.016</td>
<td>0.019</td>
<td>0.021</td>
</tr>
<tr>
<td>(D_f(±0.2))</td>
<td>2.58</td>
<td>2.58</td>
<td>2.58</td>
</tr>
<tr>
<td>(L_c(±0.5)(Å))</td>
<td>13</td>
<td>11.5</td>
<td>11.0</td>
</tr>
<tr>
<td>size(±5)(eq21)(Å)</td>
<td>390</td>
<td>330</td>
<td>300</td>
</tr>
<tr>
<td>size(±3)(fig22)(Å)</td>
<td>370</td>
<td>300</td>
<td>280</td>
</tr>
</tbody>
</table>

decrease with a decrease in the heterogeneity of the system. However, since the scattered intensities are weak under these experimental conditions, the results may contain more uncertainties.

The PDMS/C\textsubscript{14}H\textsubscript{38} liquid mixture was also investigated. Because this mixture shows similar behavior to the experimental scattering curves, the scattered intensity patterns were fitted well by the new model. Figures (6.21) and (6.22) give the fitting results and corresponding correlation functions for this system, respectively. The statistical parameters obtained are summarized in table 6.5. Again, the parameter \(D_f\) value of 2.6 and its temperature independence were observed. All results show the parameter \(D_f\) is indeed temperature insensitive. The correlation distances were found to be larger than those in PDMS/C\textsubscript{16}H\textsubscript{34} at the same concentration and temperature, indicating that these parameters are molecular weight dependent and also indicating the higher degree of heterogeneity in PDMS/C\textsubscript{18}H\textsubscript{38} liquid mixture.
Figure (6.21) Scattering patterns of the PDMS/C_{18}H_{38} liquid mixture (45% PDMS) at different temperatures: (a) 40°C, (b) 60°C, and (c) 70°C. Solid lines were obtained by equation (6.21).
Figure (6.22) Calculated correlation functions in terms of equation (6.20) for the PDMS/C_{18}H_{38} liquid mixture (45% PDMS) at different temperatures by using parameters in table 6.5. Temperatures are (a) 40°C, (b) 60°C, and (c) 70°C. Arrows indicate average sizes of aggregates.
6.8 FRACTAL DIMENSIONS WITH THE POWER-LAW

We have introduced a so-called fractal dimension parameter $D_f$ to the exponential-cosine correlation function and indeed obtained the fractal value of $D_f$, but we deal with it in the spirit of a controlling parameter. Thus far, we have not ascertained the dimension of the aggregate mixtures, fractal or not. According to the critical discussion by Martin and Hurd[14], if $R_g/a_0$ is large, it is unnecessary to use multi-parameter curve-fitting techniques since the fractal dimension can be extracted directly from a log-log plot of the scattered intensity versus wavevector at large wavevector. If $R_g/a_0$ is small (<10), on the other hand, it is meaningless to attempt to obtain fractal information that is not really

Figure (6.23) Log-Log plots of the scattered intensity versus wavevector for the PDMS/C$_{16}$H$_{34}$ liquid mixture (45% PDMS) at different temperatures: (a) 30°C, (b) 60°C, and (c) 78°C.
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Figure (6.24) The plot of the fractal dimension versus temperature for the PDMS/C$_{16}$H$_{34}$ liquid mixture (45% PDMS).

Figure (6.25) Log-Log plots of scattered intensity versus wavevector for the PDMS/C$_{18}$H$_{38}$ liquid mixture (45% PDMS) at different temperatures: (a) 40°C, (b) 60°C, and (c) 70°C.
there. By accepting the reasonable suggestion of Martin and Hurd [14], we determine the fractal dimension by using the power-law. If $D_f$ obtained from the power-law is a measurement of the fractal dimension, it must also reflect the degree of aggregation in the mixtures, which means that this parameter cannot be expected to be always independent of temperature in a wide range.

Figure (6.23) shows log-log plots of a PDMS/C$_{16}$H$_{34}$ liquid mixture (45% PDMS) at different temperatures. The values of $D_f$ are determined by the least-squares method. Indeed, in this figure, $D_f$ is found to be dependent on temperature rather than a constant. Within the range of the measured temperature, the values of $D_f$ span the regime 1.45-1.7 and do not agree with the results obtained from equation (6.21). As the temperature increases, the value of $D_f$ decreases, indicating that the aggregation tends to take on a sparser appearance, as expected by the computational simulation [22]. In figure (6.24), $D_f$ is plotted as a function of temperature for the same mixture. Figure (6.25) shows log-log plots of the PDMS/C$_{18}$H$_{38}$ liquid mixture (45% PDMS) at different temperatures. The power-law analysis gives the values of $D_f$ spanning the regime 2.07-1.78. Again, the temperature dependence of $D_f$ is observed, as shown in figure (6.26). It is also noted that the value of $D_f$ obtained from PDMS/C$_{18}$H$_{38}$ liquid mixture is larger than the corresponding value of PDMS/C$_{16}$H$_{34}$ rather than the same as determined by equation (6.21). It is understandable that the degree of aggregation of PDMS/C$_{18}$H$_{38}$ liquid mixtures could be larger than that of PDMS/C$_{16}$H$_{34}$ mixtures due to the longer chain length of C$_{18}$H$_{38}$. These results are also in agreement with these obtained from the statistical parameters determined by

![Figure(6.26) The plot of the fractal dimension versus temperature for the PDMS/C$_{18}$H$_{38}$ liquid mixture (45% PDMS).]
Figure (6.27) Log-Log plots of the scattered intensity versus wavevector for PDMS/C₁₆H₃₄ liquid mixtures at 40°C. Concentrations of PDMS are (a) 5.5%, (b) 10.1%, (c) 20%, (d) 40%, and (e) 50%.
Figure (6.28) The plot of the fractal dimension versus concentration (weight%) for PDMS/C\textsubscript{16}H\textsubscript{34} liquid mixtures at 40°C.

The effect of the polydispersion of an aggregate mass on the fractal dimension has been found\cite{28}. Martin and Ackerson\cite{17} have derived the following straightforward relations for mass fractal dimensioned systems with polydisperse distribution

\[ I \propto Q^{-D_f(3-\tau)} \quad \tau > 2 \]

\[ I \propto Q^{-D_f} \quad \tau < 2 \] \hspace{1cm} (6.25)

where \( \tau \) is the polydisperse exponent. As can be seen, when the exponent \( \tau \) is less than 2, the mass polydispersion does not affect the fractal dimension. The percolation theory \cite{29} gives \( \tau=2.2 \) in three dimensions, and mean-field theory gives \( \tau=2.5 \) independent of the dimension\cite{30-31}. Since the molecular weight distribution of PDMS is large, the aggregate masses in the liquid mixture of paraffin/PDMS may be not uniform but may be distributed in size. If we adopt the percolation theory, the mass fractal dimensions must be 1.25 times as large as those obtained from monodispersal considerations.

The effect of mass polydispersion on the scattered intensity may also be calculated by
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following form if the scattered intensity has a absolute unit.

\[ \Gamma'(Q) = \int_0^\infty Nn(N)I(Q)dN \]  \hspace{1cm} (6.26)

where \( N \) is the number of monomers per aggregate, \( n(N) \) size distribution. Here, we use scaling to describe the \( n(N) \).

\[ n(N) = \frac{M_i^2}{M_i} (1 - \lambda)^{(1-\lambda)} \Gamma^{-1}(1 - \lambda)(\frac{NM_0}{M_i})^{-\lambda} \exp[-(1 - \lambda)(\frac{NM_0}{M_i})] \]  \hspace{1cm} (6.27)

where \( M_i \) is the \( i \)th moment, \( \Gamma \) is the gamma function. \( \lambda \) is an adjust parameter and a function of \( D_f \). By substituting equations (6.21) and (6.27) into equation (6.26), we have

\[ \Gamma'(Q) = (1 - \lambda)^{-2} \frac{\Gamma(3 - \lambda)}{\Gamma(1 - \lambda)} \frac{M_i^2}{M_0} I(Q) \]  \hspace{1cm} (6.28)

In practice, since the scattered intensity has been scaled into a constant when we calculate \( I(Q) \) with equation (6.21), the polydisperse effect has been included.

Our results can be compared with some aggregation models. The cluster-cluster model[24-25], which allows many clusters to form and to aggregate among themselves, produces \( D_f = 1.75-1.8 \) in three dimensions. The simulation for cluster-cluster diffusion limited and reaction-limited aggregation yields \( D_f = 1.7-2.0 \)[26-27]. The Witten-Sander(WS) model, in which single diffusing particles aggregate onto a growing cluster, produces \( D_f = 2.56 \) for three dimensions and \( D_f = 1.38-1.45 \) for two dimensions. In these models, the particles are dilute, and until they stick together irreversibly on contact, noninteracting. The values of \( D_f \) obtained in this work could be qualitatively in agreement with cluster-cluster models, but we can not confidently claim the presence or absence either of these two limiting behaviors. At 78°C, the \( D_f \) value of about 1.45 was observed for the PDMS/C_{16}H_{34} liquid mixture. Whether this means the dimension of aggregates could approach two is not clear. However, it is beyond question that the lower value of \( D_f \) reflects the more stringy appearance of aggregates.

6.9 CONCLUSIONS

A new correlation function in the form of

\[ \gamma(r) = r^{(D-D_f)} \exp(-r/a_0)\cos(br) \]
was presented to describe the essential features of aggregate structure by considering the effects of partial ordering and deviation from Porod’s law on the scattering curves. The scattered intensity distribution corresponding to this correlation function was obtained by Fourier transformation. The new scattering formula, with three parameters, can predict a peak in smaller wavevectors and can control the scattered intensity decay in larger wavevectors. Therefore, this model, compared with existing ones, can satisfy the whole wavevector ranges. The nature of the fractal behavior may be contained in the parameter $D_f$, but $D_f$ is herein considered to be a controlling parameter rather than a fractal dimension. The fractal dimension is preferentially determined from the power-law. The experimental scattering curves obtained from PDMS/paraffin liquid mixtures were fitted very well by the new model within experimental errors with three parameters. The relationship between the fractal dimension and the degree of aggregation has been discussed. The new model includes features of existing models and would be extended to systems with similar scattering patterns.
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6.10 REFERENCES

4. G. Porod, Kolloid Z. 124, 83 (1951)
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27. P. Meakin, J. Colloid Interface Sci. 102, 505 (1984)
30. P. Flory, J. Am. Chem. Soc. 63, 3083 (1941)
32. P. Van Dongen and M. Ernst, Phys. Rev. Lett. 54, 1396 (1985)
CHAPTER SEVEN GENERAL CONCLUSIONS

In this thesis, aggregation and disaggregation phenomena have been extensively studied by using small angle x-ray scattering (SAXS) and neutron scattering (SANS). Two binary mixtures, binary paraffin solid solutions and PDMS/paraffin liquid mixtures, were chosen as model systems for comparison with metal alloys, polymer blends, lipid biomembranes, and colloidal solutions. The phenomena of aggregation and disaggregation occur in completely different environments for the both model systems. For the binary paraffin solid solutions, the mixing and demixing take place in a highly crystalline, randomly oriented solid. In contrast, for the PDMS/paraffin mixtures, the aggregation takes place in a spatially isotropic liquid. The relevant conclusions have been independently given in the previous Chapters. In this Chapter, the principal findings are summarised.

The demixing in unstable solid solutions was studied by rapidly quenching the mixtures from the melt to the temperatures below 45°C. No microphase separation was detected for the mixture slowly cooled and not aged. The kinetics of microphase separation in C30/C36 mixtures was tested against several dynamic scaling functions, the result indicating that the time evolution of the demixing in the present system is similar to that found in metal alloys and polymer blends. In other words, the system is initially unstable or metastable and starts to undergo a spontaneous ordering process, leading first to growth of small clusters of ordered domains, and later to coarsening of domains, which finally approach a uniformly ordered equilibrium state. It has been also found that the microphase kinetics in C30/C36 mixtures follows a logarithmical growth law, and the exponent depending on the temperature and concentration. If we accept the physical meanings of logarithmical growth law, the results indicate that the vacancies and conformational disorder have the same effect on the microphase kinetics as diffusive impurities. Accordingly, we have suggested that vacancies or conformational ordering as well as their mobility, accumulation and trapping play a crucial role in the microphase separation.
Chapter 7 General Conclusions

The time required for the sample with more long chains to reach an equilibrium is shorter than that for the sample with fewer. The dependencies of the demixing rate on the concentration ratio and the temperature are associated with the degree of conformational ordering. The effects of the vacancies or conformational ordering on the microphase separation are again demonstrated. The apparent activation energy for demixing obtained was found to be about 58 kJ/mol. Accordingly, the possible diffusion mechanism of the present system could be one intermediate between the pure vacancy and reptation models, in contrast to other systems such as polymer blends. In other words, the paraffin molecule chains could move in the partial vacancies by wriggling along their axes. The movement of the chains is constrained in an oriented medium (longitudinal direction) and accompanied with the conformational ordering. The kinetics of microphase separation is also described by Cahn's model.

The demixing occurs immediately after the quench and the average size of separated domains reaches an equilibrium state within the time scale of experiments. However, it has been found that the demixing in the present system can proceed slowly at room temperature for a very long time. The system is therefore always in a nonequilibrium state. After initial ordering, there is a process associated with a better stretching of paraffin molecule chains and further elimination of the vacancies both inside the domains and boundary regions. Also, the molecule chains overlapping two domains could be rearranged. Consequently, the morphology of the system tends to be a perfectly domain-separated structure which can be described by the paracrystalline model. In the maximum aged time (near one year), the structure was found not to be the completely separated domains. There is a correlation between the domains in the longitudinal direction. For the 1:1 mixture, the equilibrium structure is found to be an alternating arrangement of pure components. For samples unbalanced in the concentration, the average sequences of separated domains in a period are not strictly arranged in terms of the molar ratios.

At the same temperature, the time required for the D/H pair to reach an equilibrium is shorter than that for the H/D pair. The dependence of the demixing rate on the isotopic effect is due to the differences in the chain volumes and melting points between two components. For the present system, the driving force of the microphase separation is mainly determined by these differences. It has been found that the microphase separation
Chapter 7 General Conclusions

in the D/H pair becomes a two-step process, i.e., the precipitation of some pure H component advances on the separation of H and D components from a mixing state. The domain shape in the D/H pair is therefore more asymmetry.

The demixed binary paraffin mixtures are significantly thermally unstable. When the demixed $C_{30}H_{62}/C_{36}D_{74}$ mixture is slowly heated to a few degrees above room temperature, the separated domains begin to mix. The smaller domains should be dissolved first because of inherently less stable. The mixing is sharply increased and the separated domains are almost entirely dissolved when the temperature of the mixture approaches $45^\circ C$. This temperature is independent of the concentration and the isotopic effect. The mixing process is associated with the chain mixing and with the conformational disordered. These two processes are interdependent when the temperatures is lower than $45^\circ C$. However, the conformational disorder remains when the chain mixing has been largely completed. The mixing process may proceed as the temperature is further increased until the conformational disordered reaches a new free energy minimum which is associated with the randomly mixed solid solution. Because the temperature range covered begins at room temperature and extends to the melting point, the mixing should involve the orthorhombic-hexagonal transition. For the $C_{30}D_{62}/C_{36}H_{74}$ mixture, the mixing process is similar to that of $C_{30}H_{62}/C_{36}D_{74}$. However, because the domains, mainly being made up pure $C_{36}H_{74}$ component, stack above one another to form larger and more stable domains, the randomly mixed solid solution is obtained only when the temperature is increased to the melting point of pure $C_{36}H_{74}$ component. The dissolution kinetics of the separated domains can be approximated by Summerfield-Ullman model.

It is generally accepted that there are two limiting regimes of aggregation: (1) diffusion-limited cluster aggregation (DLCA), in which every collision between particles results in the formation of a permanent contact, and (2) reaction-limited cluster aggregation (RLCA), in which only a small fraction particle collisions leads to the formation of a contact. Although these two models have different values for the fractal dimension and different behavior for the kinetics of growth, both theory and experiment have shown that the two models share a common feature in that during the growth process, clusters are randomly positioned in space and there is no correlation between clusters at any time.
Chapter 7 General Conclusions

However, it has been found that the PDMS/paraffin mixtures do produce some kind of ordering between the clusters. In fact the scattered intensity distribution displays a pronounced peak at a finite wavevector. A new correlation function was therefore presented to describe the essential features of aggregate structure of PDMS/paraffin mixtures by considering the effects of partial ordering and deviation from Porod’s law on the scattering curves. The experimental scattering curves of PDMS/paraffin mixtures were fitted very well by the new model within experimental errors with three parameters. The new model includes features of existing models and would be extended to systems with similar scattering patterns.