1.1. Introduction

Neutron scattering is a standard tool when dealing with the microscopic properties of the condensed matter at the atomic level. This comes from the fact that the neutron matches with the distances and energy scales, and thus with the microscopic properties of most solids and liquids. Neutrons, with wavelengths in the order of angstroms, are capable of probing molecular structures and motions and increasingly find applications in a wide array of scientific fields, including biochemistry, biology, biotechnology, cultural heritage materials, earth and environmental sciences, engineering, material sciences, mineralogy, molecular chemistry, solid state and soft matter physics.

The striking features of neutrons can be summarized as follows. Neutrons are neutral particles. They interact with other nuclei rather than with electronic clouds. They have (de Broglie) wavelengths in the range of interatomic distances. They have an intrinsic magnetic moment (a spin) that interacts with the unpaired electrons of magnetic atoms. Their mass is in the atomic mass range. They carry, thus, similar energies and momentum than those of condensed matter, and more specifically of gas hydrates.

As gas hydrates are mainly constituted of light elements (H, O, C, etc.), in situ neutron scattering appears as a technique particularly suited to their study. In the case of diffraction (i.e. structural properties), while the identification of these light atoms by X-ray diffraction requires the presence of heavy atoms and is therefore extremely complicated, neutron diffraction (NP) is highly sensitive to them due to the interaction of the neutrons with nuclei rather than with electron clouds. Moreover, most of the matter is
Gas Hydrates 1

“transparent” to neutron beams. Such a feature provides advantages for studying gas hydrates when a heavy sample environment is required (e.g. high pressure, low temperature). For instance, X-ray powder diffraction studies are usually restricted to small sample volumes, as large sample volumes would be associated with a strong absorption and unwanted scattering from the pressure cell. Neutron techniques allow studies of bulk processes in situ in representative volumes, hence with high statistical precision and accuracy [STA 03, HEN 00, GEN 04, FAL 11]. Furthermore, although alteration of some types of ionic clathrate hydrates (or semiclathrates), such as the splitting of the tetra-alkylammonium cations into alkyl radicals [BED 91, BED 96], by X-ray irradiation has been reported, neutrons do not damage sample.

Finally, future developments in gas hydrate science will be based on the understanding, at a fundamental level, of the factors governing the specific properties of gas hydrates. In this respect, the investigation of gas hydrate dynamics is a prerequisite. At a fundamental level, host–guest interactions and coupling effects, as well as anharmonicity, play an important role. These phenomena take place over a broad timescale, typically ranging from femtoseconds to microseconds. Investigating the dynamics (intramolecular vibrations, Brownian dynamics, etc.) of gas hydrates thus requires various complementary techniques, such as NMR or Raman spectroscopy, and indeed inelastic and quasi-elastic neutron scattering (QENS), especially when it comes to encapsulating light elements such as hydrogen or methane in water-rich structures.

In this chapter, the recent contributions of neutron scattering techniques in gas hydrate research are reviewed. After an introduction to neutron scattering techniques and theory, an overview of the accessible information (structural and dynamical properties) by means of neutron scattering is provided. Then, selected examples are presented, which illustrate the invaluable information provided by neutron scattering. Some of these examples are directly related to existing or possible applications of gas hydrates.

1.2. Neutron scattering

Both nuclear and magnetic neutron interactions are weak: strong but at very short length scale for the nuclear interaction and at larger scale for the magnetic interaction. In that respect, the probed sample can be considered as transparent to the neutron beam. This highly non-destructive character combined with the large penetration depth, both allowed because of the weak scattering, is one of the main advantages of this probe.

Nuclear scattering deals with nuclear scale interaction and hence presents no wave vector dependent form factor attenuation allowing to offer high momentum
transfers for diffraction or specific techniques such as deep inelastic neutron scattering (also known as neutron Compton scattering).

Neutron spectroscopic techniques range from the diffraction of large objects using small-angle scattering, usually made with long incident wavelengths (cold neutrons), to direct imaging through contrast variation (neutron tomography), usually made with short wavelengths (hot neutrons) and going through ordinary diffraction and inelastic scattering in the intermediate wavelength range.

In that respect, neutron scattering complements without necessarily overlapping the other available spectroscopic techniques such as nuclear magnetic resonance (NMR). If one naturally thinks about X-ray for structure determination, neutrons are very competitive for inelastic scattering and even essential for magnetic scattering both in the diffraction and inelastic modes.

The main drawback that contrasts with the numerous advantages comes from the intrinsic relative flux limitation of neutron sources, and thus, this type of spectroscopy can only be performed at dedicated large-scale facilities.

1.2.1. A basic ideal scattering experiment

In a generic experiment (Figure 1.1), a beam of monochromated neutrons with single energy \( E_i \) is directed on a sample. The scattered neutrons are collected along direction (angles \( \theta \) and \( \phi \)) and analyzed by energy difference with the incident energy by using a detector, covering a solid angle \( \Delta \Omega \) of the sphere, which measures the analyzed neutron intensity. The measured intensity in the solid angle spanned by the detector and in a final energy interval \( \Delta E_f \) in this simple gedanken experiment reads:

\[
I = \Phi \eta \frac{d^2 \sigma}{d \Omega d E_f} \Delta \Omega \Delta E_f
\]

[1.1]

where \( \Phi \) stands for the incident flux at the incident energy and \( \eta \) is the efficiency of the detector. The quantity between the identified terms is the double differential scattering cross-section, a surface per unit of energy, which characterizes the interaction of the neutron with the sample or the surface that the sample opposes to the incident beam. Since the intensity has the dimension of count/s, the double differential scattering cross-section can be seen as the ratio of the scattered flux in the given detector per unit energy over the incident flux.
1.2.2. Neutron scattering theory

The mathematical development of the neutron scattering technique comes from the more general scattering theory. The interaction of the neutron with a single nucleus is first examined and then the generalization of the theory for an assembly of scatterers is developed. From scattering theory to its application to neutron scattering, the aim is to convince that the scattering of neutrons by the nuclei or by the spins of an ensemble of atoms provides information on the structure and motions of the atoms, i.e. information on the sample under investigation at the atomic level.

To study the scattering of a single neutron by one nucleus of the sample at the atomic level, one has to consider the incoming neutron as a plane wave, whose square modulus gives the probability of finding the neutron at a given position in space (this probability is a constant for a plane wave). Considering a point-like interaction between the neutron plane wave and the nucleus, the nucleus size in interaction being far smaller than the neutron wavelength and atomic distances, the scattered neutron wave is then described as an isotropic spherical wave whose intensity is proportional to $1/r$ and the strength of the interaction between the neutron and the nucleus of interest, called the scattering length $b$.

The scattering length $b$ is specific (and tabulated, see [SEA 92]) to each nucleus and does not vary with the atomic number in a correlated way. It can be positive, meaning repulsive interaction, negative (attractive) and can be complex and energy
dependent, which means that the target can absorb the neutron (absorption proportional to the incident wavelength in the thermal neutron range).

Going from the scattering by a single nucleus to the scattering by a macroscopic assembly of nuclei as found in a condensed medium is a matter of properly summing all scattered waves under well-defined approximations, which are generally fulfilled in neutron scattering experiments.

The first obvious approximation is that the scattered waves are weak and thus leave the incident plane wave unperturbed over the coherence volume. This allows retaining only the first term of the Born series of the Lipmann–Schwinger equation. This simplification is known as the Born approximation.

For the sample (but not for the sample nuclei whose states are left unchanged), the neutron is a perturbation, and then the scattering can be treated within perturbation theory. At the quantum level, during the interaction of the neutron with a nucleus of the sample, the sample is changing from an initial state $\lambda_i$ to a final state $\lambda_f$ (which are left undefined so far but depends on the system under consideration) via the interaction potential $V(r)$. The point-like interaction potential $V_f(r)$ is known as the Fermi pseudo-potential and reads, with normalization factors:

$$V_f(r) = \frac{2\pi\hbar^2}{m_n} b_j \delta(r - r_j)$$

[1.2]

where $m_n$ is the neutron mass ($1.675 \times 10^{-27}$ kg) for an atom with scattering length $b_j$ at position $r_j$. Conservation laws tell us that the change in energy $\hbar\omega = E_f - E_i$ and momentum $Q = k_f - k_i$ of the probe (the neutron) should be reflected in a similar change in the quantum state of the target.

In the language of quantum mechanics, the summation over the scattered waves is equal to a sum over the final quantum states $\lambda_f$ while averaging over the statistically weighted initial states of the system. The statistics of the initial state $p_{\lambda_i}$ is taken as a Boltzmann distribution, from which other statistics can be deduced depending on the quantum nature of the target (bosons or fermions).

The calculation is rather cumbersome but robust within the framework of the approximations valid in ordinary neutron scattering. The theory is extensively described in dedicated books [SEA 92, LOV 84]. One ends up then with the definition of the double differential cross-section, the quantity directly measured in a scattering experiment:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} S(Q, \omega)$$

[1.3]
The scattering function \( S(Q, \omega) \) or dynamical structure factor reads:

\[
S(Q, \omega) = \frac{1}{2\pi\hbar} \sum_{jj'} b_j b_{j'} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \langle e^{-iQr_j(0)} e^{iQr_{j'}(t)} \rangle
\]  \[1.4\]

It is a function that depends solely on \( Q \) and \( \omega \) for the neutron and that contains all the probed dynamics of the target in the double sum over the Fourier transform of the thermal average of the expectation value of the product of some Heisenberg operator \( e^{iQr_j(t)} \) (which do not commute, except in the classical limit), i.e. the term between angular brackets.

### 1.2.3. Correlation functions

At this stage, one can be puzzled about the significance of the time Fourier transform of the operator expectation value where all summations and averages over the quantum states of the sample have been condensed in this compact but not very meaningful expression.

Fortunately, van Hove [HOV 54] derived the above expression in terms of intuitive number density pair correlation functions between the atom labeled \( j \) at position \( r_j(0) \) at initial time \((t = 0)\) and another atom \( j' \) at position \( r_{j'}(t) \) at time \( t \).

To simplify the discussion, the nucleus-dependent scattering length is usually reduced to a single value \( \Delta = \Delta \) and removed from the summation in \[1.4\]. The number density operator reduces here to the sum over the atoms of the sample of the point-like probability of finding a scatterer at position \( r_j(t) \) at time \( t \):

\[
\rho(r, t) = \sum_j \delta (r - r_j(t))
\]  \[1.5\]

Defining the autocorrelation in space and time of the number density operator:

\[
G(r, t) = \int d^3r' \langle \rho(r - r', 0) \rho(r', t) \rangle
\]  \[1.6\]

and using the space Fourier transform of a delta function:

\[
\frac{1}{(2\pi)^3} \int d^3r \, e^{-iQr} \delta(r - r_j(t)) = e^{iQr_j(t)}
\]  \[1.7\]

leads to:

\[
G(r, t) = \frac{1}{(2\pi)^3} \int d^3Q \, e^{-iQr} \sum_{jj'} \langle e^{-iQr_j(0)} e^{iQr_{j'}(t)} \rangle
\]  \[1.8\]
that is, once plugged into [1.4]:

\[ S(Q, \omega) = \frac{b^2}{2\pi\hbar} \int d^3r \int dt \, e^{i(Qr-\omega t)} \, G(r, t) \quad [1.9] \]

The scattering function is thus the time and space Fourier transform of the number density or pair correlation function \( G(r, t) \). In the classical approximation (usually when \( kT \gg \hbar\omega \)), \( G(r, t) \) can be defined as the probability that, given a particle at the origin of time \( t = 0 \), any particle is within the elementary volume \( dr \) around the position \( r \) at time \( t \).

\( G(r, t) \) is a physical quantity that can be derived from analytical models or from molecular dynamics (MD) calculations. With such models, a direct comparison with the results of a scattering experiment, i.e. \( S(Q, \omega) \), is thus possible. It has to be noted, however, that the sample can contain several atoms species and thus different scattering lengths \( b_j \) that render the interpretation more difficult even if the trend is the same. In particular, reversing the Fourier transform to deduce the correlation functions from the scattering function is not straightforward because information is lost in the superposition of contributions of different scattering lengths.

The partial space Fourier transform, the term under the sum in [1.4] or [1.8], is also called the intermediate scattering function and one can go back and forth from \( S(Q, \omega) \) to \( G(r, t) \) via the intermediate step \( I(Q, t) \):

\[ I(Q, t) = \sum_{jj'} \langle e^{-iQr_j^{(0)}} e^{iQr_j^{(t)}} \rangle = \frac{1}{(2\pi)^3} \int d^3r \, e^{iQr} G(r, t) \quad [1.10] \]

As a final remark of this section, it is important to note that the expression [1.9] summarizes the direct relationship existing between classical or \textit{ab initio} MD simulations and neutron scattering experiments: the atomic trajectories, computed by means of simulations, can be “simply Fourier transformed” in time and in space, to calculate a simulation-derived scattering law, directly comparable with the experimental one, as it will be illustrated in this chapter.

### 1.2.4. Coherent and incoherent scattering

When coming back to the scattering length one has to note an additional difficulty, which can be in fact taken as an advantage. The scattering length \( b_j \) of the nucleus are randomly distributed on the chemical species. This random distribution is due to the isotopic nature of the nuclei. Since it does not affect the chemical properties, the different nuclei isotopes in the sample, each with a different scattering length, are randomly distributed. A second “randomization” comes from the spin interactions in the system neutron plus nucleus during the interaction. The
neutron spin from an unpolarized neutron beam couples randomly with the nucleus spin during the interaction and since the scattering length depends on the way the spins couple with each other, it leads to another source of randomization of the effective scattering length in the sample under study.

There is, however, a convenient way of dealing with this problem at an ensemble average level without taking care of the microscopic (atomic) level of the problem.

Starting from equation [1.4], one can rewrite the expression:

\[ S(Q, \omega) = \sum_{jj'} b_j b_{j'}^* S_{jj'}(Q, \omega) \]  \[\text{[1.11]}\]

to emphasize the scattering length visualization. Keeping the monoatomic sample, the indices carry on the atomic positions but not on the different scattering lengths due to isotopes or spin-interactions. Because the difference in energy or momentum of the scattered neutrons does not change when interacting with different isotopes or neutron–nucleus spin interactions\(^1\), one can take the average over the scattering lengths:

\[ S(Q, \omega) = \sum_{jj'} \overline{b_j b_{j'}^*} S_{jj'}(Q, \omega) \]  \[\text{[1.12]}\]

and because the nuclear spin and the isotopes are not correlated between sites \(j\):

\[ \overline{b_j b_{j'}^*} = \overline{b_j^2} \quad \text{if } j \neq j' \]  \[\text{[1.13]}\]

\[ \overline{b_j b_{j'}^*} = \overline{b_j^2} = \overline{b_{j'}^2} \quad \text{if } j = j' \]  \[\text{[1.14]}\]

or, in a compact notation with transfer of the \(j' = j\) term on the left-hand term on the right-hand side of the equality:

\[ \overline{b_j b_j^*} = \overline{b_j^2} + \left( \overline{b_j^2} - \overline{b_j^2} \right) \delta_{jj'} \]  \[\text{[1.15]}\]

which, plugged into equation [1.12], gives:

\[ S(Q, \omega) = \sum_{jj'} \overline{b_j b_{j'}^*} S_{jj'}(Q, \omega) + \sum_j \left( \overline{b_j^2} - \overline{b_j^2} \right) S_{jj}(Q, \omega) \]  \[\text{[1.16]}\]

The first term represents the sum of all possible pairs of atoms \((j, j')\), each term representing a two-body correlation between the positions of atom \(j\) at time 0 and atom \(j'\) at time \(t\). It contains interference terms in the scattering and gives rise to \textit{coherent scattering}. The second term represents the sum of all atoms \(j\) at one time, each term representing a correlation between the position of atom \(j\) at time 0 and that of the same atom at time \(t\), that is, \textit{incoherent scattering}, sensitive to single-particle

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\(^1\) There are noticeable but scarce counterexamples, the para-/ortho-hydrogen (H\(_2\)) is the most known.
spatiotemporal correlations. Incoherent scattering arises thus from the random distribution of scattering lengths about the mean, as schematized in Figure 1.2. As shown by equation [1.16], both scattering occur at the same time during an experiment, whereas they have substantially different origin. For nuclei carrying coherent and incoherent scattering lengths or cross-sections, the Bragg peaks from coherent scattering are superimposed to an unstructured incoherent background reflecting the summation of the two contributions. In inelastic scattering, if the summation still holds, it is not always simple to discriminate between both contributions, at least in simple experiments without polarization analysis.

Figure 1.2. Sketch of the separation coherent/incoherent. A single atomic sample with three isotopes (problem reduced to the static part of the isotopes here) is split in its average scattering length $\bar{b}$ on all nuclei plus the fluctuations around the mean value for each nucleus ($b_j^2 - \bar{b}^2$). For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip

Fortunately, there are some degrees of freedom with the scattering lengths themselves. Some atomic species are dominated by a single isotope and, moreover, some have no nuclear spin. In the case, for example, with $^{12}$C or $^{16}$O, $b_j = b$ for all $j$, $\bar{b}^2 = \overline{b^2}$ and thus the incoherent scattering term vanishes. They are then pure coherent scatterers. On the other hand, atoms as simple as the hydrogen have weak coherent scattering length but are dominated by the spin incoherence and thus the scattering is dominated by the incoherent scattering and the coherent scattering is vanishingly negligible. Substituting the $^1$H isotope with the $^2$H (deuterium) isotope is largely used (although it might become expensive in certain cases) to inverse completely the problem: in this case, the coherent scattering largely dominates. Depending on the information one wants to get out of the experiment, ensemble average of individual properties or collective atoms interdependent positions and dynamics, one can switch between these two sides of the same coin. In intermediate cases, where the system under study is neither a pure coherent nor an incoherent scatterer, it is still possible to make an isotope substitution to label the contribution of specific atoms in the scattered intensity either in the coherent or incoherent spectra. In this case, the shift in energy due to the isotopic substitution of the excitations that are proportional to the square root of the masses can also be directly measured at the same time on light atoms.
To better separate the two contributions, the expression in equation [1.16] can be written as:

\[ S(Q, \omega) = S_{coh}(Q, \omega) + S_{inc}(Q, \omega) \]  

[1.17]

and depending on the dominant contribution, one can get rid of one of the terms on the right-hand side.

Within the crude simplification of a monoatomic sample, \( \bar{b}_j^2 \equiv \bar{b}^2, \bar{b}_j^2 = \bar{b}^2 \), the indices over the positions drop off because they are all the same, the scattering function can be expressed in terms of coherent and incoherent scattering \textit{cross-sections}: \( \sigma_{coh} = 4\pi \bar{b}^2 \) and \( \sigma_{inc} = 4\pi (\bar{b}^2 - \bar{b}^2) \):

\[ S_{coh}(Q, \omega) = \frac{\sigma_{coh}}{4\pi} \sum_{jj'} \int dt \ e^{-i\omega t} \left( e^{-iQr_{j}(0)} e^{iQr_{j'}(t)} \right) \]  

[1.18]

\[ S_{inc}(Q, \omega) = \frac{\sigma_{inc}}{4\pi} \sum_j \int dt \ e^{-i\omega t} \left( e^{-iQr_{j}(0)} e^{iQr_{j}(t)} \right) \]  

[1.19]

from which the coherent and incoherent intermediate scattering functions (equation [1.10]) and correlation functions (equation [1.8]) can be deduced. The splitting in equations [1.18] and [1.19] emphasizes that in the former we have a sum over the correlation functions of all pairs of atoms \((j,j')\) at different times, whereas in the latter we have a summation over all same atoms \(j\) at different times.

<table>
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<th>c (%)</th>
<th>( b_c ) (fm)</th>
<th>( b_i ) (fm)</th>
<th>( \sigma_c )</th>
<th>( \sigma_i )</th>
<th>( \sigma_c )</th>
<th>( \sigma_a )</th>
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<td>(^1\text{H})</td>
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<tr>
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</table>

\textit{Table 1.1. Examples of scattering lengths (}\( b \)\textit{ in fm) and cross-section (}\( \sigma \)\textit{ in barns) for some selected chemical species [SEA 92]}

Natural hydrogen (H) is made essentially of \(^1\text{H}\) and thus is a pure incoherent scatterer. The incoherent cross-section is so large that, at any time in an organic sample, containing thus a large proportion of hydrogen, the hydrogen dominates the scattering unless an isotope substitution with deuterium is made. Carbon (C) is a pure coherent scatterer: no nuclear spin and an almost single isotope. In contrast to
this, the vanadium (V) is essentially an (spin) incoherent scatterer. Its spatial flatness response is often used for instrument calibration. Many others atoms are less selective in their affinity, e.g. sodium (Na) has one isotope and almost equal incoherent and coherent scattering cross-sections. A large benefit could be obtained from the high sensitivity of hydrogen in clathrate hydrate: contrast between the scattering response of the cages and the guest molecules could be reached by selectively deuterating the cages and/or the guest molecules.

1.2.5. A simple example of scattering

A simple example of incoherent scattering and self-correlation function is given by following a particle experiencing Brownian motion in a fluid. The canonical example of this situation is the argon atom in liquid argon [SKO 72] that exhibits both coherent and incoherent scattering. The particle has to obey the Fick law of diffusion due to thermal agitation and successive strokes on the particle in the medium.

In the classical limit, the self-correlation function $G_s(r, t)$ is a solution of the Fick equation (second Fick’s law or standard diffusion equation) with the self-diffusion coefficient $D_s$:

$$G_s(r, t) = \left(\frac{1}{4\pi D_s t}\right)^{3/2} e^{-\frac{r^2}{4D_s t}}$$  \[1.20\]

from which can be deduced the self-intermediate scattering function by space Fourier transform:

$$I_s(Q, t) = e^{-D_s Q^2 t}$$  \[1.21\]

and thus the incoherent scattering function, the quantity directly measured in a neutron scattering experiment, by time Fourier transform is:

$$S_{inc}(Q, \omega) = \frac{1}{\pi} \frac{D_s Q^2}{\omega^2 + (D_s Q^2)^2}$$  \[1.22\]

The measured incoherent spectrum of an ensemble of individual particles obeying the Fick law is a Lorentzian depending on $Q = |Q|$ and $\omega$.

Some properties of the scattering functions arise from this simple example. First, $\int S_{inc}(Q, \omega) d\omega = I_s(Q, t = 0) = 1$. The incoherent scattering function is normalized whatever $Q$, and thus the energy-integrated scattering appears as a flat-in-$Q$, unstructured, intensity\(^2\) as expected from the summation over unrelated

\(^2\) The Debye–Waller term that comes from atomic vibrations in front of the scattering functions is neglected here.
contributions. In terms of correlation function, the probability of finding the particle at initial position \( r \) at time \( t = 0 \) should be 1: \( G_s(r, t = 0) = \delta(r) \) and at infinite time, the probability of finding the particle at the same place \( r \) (in the elementary volume \( dr \) to be more precise) should be the inverse of the explored volume \( V \); in the liquid case, the entire volume of the sample is given as: \( G_s(r, t \to \infty) = 1/V. \)

**Figure 1.3.** Self-correlation function, intermediate scattering function and dynamical structure factor for the simple case of a self-diffusion of a particle with diffusion coefficient \( D = 10^{-5} \) cm\(^2\)/s. For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip

In the opposite case, the coherent scattering should show the liquid-like structure factor when integrated over the energy: \( \int S_{coh}(Q, \omega) d\omega = S(Q) \) and \( G_d(r, t \to \infty) = \rho \), the limit at infinite time of the pair correlation function (\( d \) stands for distinct) is the average particle density \( \rho \). The coherent scattering functions are more difficult to obtain, even for a simple liquid: a derivation can be found in [HAN 06]. Neglecting the viscosity, thus transverse terms, one ends up with the intermediate scattering function from the number density pair correlation:

\[
I_d(Q,t) = \langle \rho_Q(t) \rho_{-Q}(0) \rangle = \left( \frac{\gamma-1}{\gamma} \right) e^{-D_T Q^2 t} + \frac{1}{\gamma} e^{-Q^2 t \cos(v_s Q t)} \tag{1.23}
\]

where \( \gamma = C_p/C_V \) is the specific heat ratio. The expression [1.23] shows an exponential decay, as in the self-diffusion, but with a thermal transport coefficient \( D_T \) different from the self-diffusion coefficient, and a damped oscillatory function, whose frequency depends on the speed of sound \( v_s \) in the liquid. The time Fourier transform is analytically simple:

\[
S_{coh}(Q, \omega) = \frac{S(Q)}{2} \left[ \left( \frac{\gamma-1}{\gamma} \right) \frac{2D_T Q^2}{\omega^2 + (D_T Q^2)^2} + \frac{1}{\gamma} \frac{Q^2}{(\omega + v_s Q)^2 + (Q^2)^2} + \frac{Q^2}{(\omega - v_s Q)^2 + (Q^2)^2} \right] \tag{1.24}
\]

In addition to the Rayleigh line centered at \( \omega = 0 \), a collective excitation, the (longitudinal) sound wave, a density wave, occurs in the liquid. Equation [1.24] is an approximation at low \( Q \), in particular, the central Lorentzian width does not show up the so-called “De Gennes narrowing”, an increase in the (pair) correlation times.
(narrowing of the Lorentzian width) at the maximum of $S(Q)$ corresponding to first neighbor distances due to favorable local arrangement. This can be overcome in a first approximation by replacing the Lorentzian width by $D_q Q^2 / S(Q)$.

![Figure 1.4. Coherent structure factor of liquid sodium (left). Sketches of intermediate and coherent scattering functions for the coherent case. For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip](image)

The example of monoatomic liquids illustrates the power and weaknesses of inelastic neutron scattering. Self-correlations and pair-correlations give access to different properties of the liquid. Thus, through isotope substitution (when possible) or polarization analysis, the neutron beam behaves as a dual probe.

When dealing with diffusion and relaxation in incoherent scattering, many meaningful microscopic models exist or are easy to imagine; the passage to the scattering law that can be compared to the measurements being rather straightforward [BEE 86]. This holds for all systems where incoherent cross-sections are dominant in the scattering. Even in the monoatomic liquid case, deriving the coherent scattering from the particle density correlations is a difficult step and cannot be usually derived from scratch each time a new compound is being studied. Fortunately, neutron scattering has allowed for many correlation functions or scattering functions of practical interest to be derived. Within approximations or “hacking” of known models, it is possible to adapt each new case to the known theoretical material. In the case of more complex materials, e.g. molecular materials with several chemical species where the superposition of scattering from heterogeneous scattering lengths apply, understandable analytical models are not always possible. In particular, it is not possible to Fourier transform the scattering function $S(Q, \omega)$ to get the correlation functions $G(r, t)$ as it is feasible, although rarely used, in a mononuclear system.

A frequent approach for a complex system involves MD calculations. The quantities of interest can be inferred from the molecular dynamic trajectories and
velocities and, moreover, a specific labeling of the atoms in the system under study *in silico* allows to extract more accurately the role of the constituents in a molecular system. MD is another way of obtaining the emergent physics at a macroscopic scale from simpler modeling, although not that simple with *ab initio* calculations, at a microscopic level. From the recorded trajectories, the mean-square displacement can be directly computed from the ensemble average of the distances of a tagged particle:

\[
\langle u^2(t) \rangle = \frac{1}{N} \langle \sum_j |r_j(t) - r_j(0)|^2 \rangle
\]  

[1.25]

In the long time limit, the macroscopic self-diffusion coefficient \( D_s \), the same as in the example above, can be computed as:

\[
D_s = \lim_{t \to \infty} \frac{\langle u^2(t) \rangle}{6t}
\]  

[1.26]

It is also possible to compute various kinds of correlation functions. In particular, the velocity autocorrelation function defined as the projection of the velocity at time \( t \) onto the initial velocity averaged over the initial conditions:

\[
C(t) = \frac{1}{3} \langle \mathbf{v}(t), \mathbf{v}(0) \rangle
\]  

[1.27]

has important properties. At \( t = 0 \), \( C(t) = 1/3 \langle \mathbf{v}^2(0) \rangle = k_B T / m \) because of the equipartition of the energy, giving access to the temperature of the system under simulation. Another important equation is the relation between the velocity autocorrelation function and the self-diffusion coefficient:

\[
D_s = \int_0^\infty C(t) dt
\]  

[1.28]

This equation constitutes an example of a Green–Kubo formula relating a macroscopic property in terms of the time integral over a microscopic time–correlation function. From the trajectories, the van Hove correlations can also be computed, and thus the intermediate and scattering functions, which can be directly confronted to neutron measurements.

### 1.3. Probing structural and dynamical properties of gas hydrates

The host substructure of a clathrate hydrate is constituted with a slightly distorted tetrahedral distribution of water molecules. An ideal clathrate hydrate includes a distribution of the H-bonds within the water substructure, respecting the ice rule, i.e. each water molecule accepts and donates two hydrogen bonds. The dynamic and static proton disorder in the H-bond subsystem is typical of most
polymorphous crystalline forms of ice. It appears because of the delocalization of the protons between the neighboring oxygen atoms and because of reorientations of water molecules. Moreover, guest molecules encapsulated within the water cages exhibit a high degree of disorder (e.g. inter- or intracage diffusion, reorientations, rattling), triggered by the host–guest interactions. Clathrate hydrates can then be considered as glassy crystals with respect to the large variety of molecular motions. Neutron scattering techniques constitute the appropriate tools for proposing comprehensive models revealing this dynamical and/or statistical disorder met in clathrate hydrates [DES 12]. This section provides an overview of the dynamical and structural properties met in clathrate hydrates. Focused examples are provided in the following sections.

1.3.1. Structures

A primary use of neutron scattering probably resides in the ability of this technique to locate light elements like hydrogen, or more specifically deuterium (see the coherent cross-section of deuterium in Table 1.1), compared to X-ray scattering. Neutron powder diffraction performed on clathrate hydrates possessing deuterated water cages give access to the proton distribution around the oxygen atoms constituting the cages. Using deuterated guest molecules (such as methane, i.e. rich in hydrogen), neutron powder diffraction provides information about the distribution of guest molecules within the cage in terms of orientational distribution or cage occupancies. The readers may find numerous structures of clathrate hydrate resolved by means of neutron powder diffraction in the literature (e.g. [SLO 08]).

**Figure 1.5.** Neutron diffraction data obtained on carbon monoxide clathrate hydrate at 260 K and at indicated pressures for various formation conditions (temperature, pressure and duration of P-T exposure) indicated on the figure (according to [ZHU 14]). For a color version of this figure, see www.iste.co.uk/bros/hydrates1.zip
Among the numerous studies dealing with structure refinement by means of NP, let us consider a few examples. A full structural refinement of NP data leads to the location of the hydrogen atom positions with high precision [HEN 00], which is especially suited for determination of the position and quantity of hydrogen (deuterium) (eg. [MUL 08]). In addition, in the case of single crystals, this technique allows the refinement of multiple cage occupancy and orientation ordering in cages (e.g. pure H₂ hydrates [LOK 04], binary H₂/THF hydrates [HES 06]).

Some remarkable results for clathrate science have been obtained by means of neutron powder diffraction (NPD) in recent years. One example is the very recent discovery of a new ice phase, referred to as ice XVI [KUH 14]. This phase is an s-II clathrate structure with empty cages, obtained after 5 days of vacuum pumping neon clathrate hydrates. Another example is the metastability of the type I structure formed with carbon monoxide guest molecules: the s-I structure is kinetically favored, but transforms into the s-II structure – thermodynamically more stable – after a few weeks [ZHU 14].

Due to the high flux available on neutron diffractometers together with its simultaneous readout over a large 2θ range and to the excellent penetration power of neutrons (allowing the use of high-pressure equipment and cryogenic devices with relative ease), in situ NPD represents a useful tool for investigating structural changes when external (e.g. pressure) conditions are variable [MAO 02]. Neutron powder diffraction is useful for clarifying the difference in the thermal vibrations of the same kind of atoms at crystallographically distinct sites [IKE 99]. Moreover, NP experiments have enabled some recent successes both in studying the clathrate hydrate kinetics of formation/decomposition [STA 03, MUR 09, KUH 06a], guest replacement reactions (especially when accompanied by a structural transition) and have also provided useful information on the time dependency of hydrate transformations [HAL 01]. Thus, neutron scattering is widely used for in situ experiments and this specificity will be illustrated in the following sections.

### 1.3.2. Relaxation of guest molecules and water molecules

Because of the exceptionally large incoherent neutron scattering cross-section, nearly two orders of magnitude greater than that of any other nucleus (see Table 1.1), incoherent QENS techniques are particularly sensitive to proton and have also emerged as invaluable tools for the study of clathrate hydrates. Indeed, as QENS gives access, in both space and time, to the individual displacements of nuclei, a detailed description of the spatial and time characteristics of diffusive mechanisms – especially in the case of hydrogen – can be obtained at a microscopic level.
The stability of the water molecules framework is ensured by the directionality of the H-bond, involving the so-called ice rule. The signature of the relative rigidity of the cages resides in the reorientational process of water molecules, exhibiting quite high activation energy in the order of 30–50 kJ·mol$^{-1}$ [SLO 08, DAV 73]. $^2$H NMR investigations reveal that the relaxation of water molecules in clathrate hydrates occurs on a microsecond timescale [BAC 01, KIR 03, SLO 08]. This characteristic time is relatively long with respect to the observation timescale (typically ranging from picoseconds to nanoseconds) probed by means of QENS experiments. Thus, the incoherent QENS spectra include an elastic-like scattering due to the water molecules, limiting the interest of this technique for probing the water Brownian motions. The process of orientational ordering and the occurrence of H-bond defects (Bjerrum defects, ionic defects, etc.) within the host network may facilitate the water molecule relaxation. These defects might be created through the existence of short lifetime (of the order of the picoseconds) H-bonds between water molecules and guest molecules [ALA 09, BUC 09, PEF 10]. Another way to generate H-bonds defects in the network of the water substructure is to confine acids within the cages. The acidic guest molecules are then enclosed within correspondingly cationic water cages in which the proton excess is delocalized [MOO 87, DES 13], leading to superprotonic conductors [SHI 10]. In such a case, QENS is the technique to elucidate the mechanism of the protonic conduction and to probe the induced modification of water relaxation. Playing with the energy resolution used in experiments (i.e. with the observation time to probe the system), QENS has enabled to disentangle the dynamics occurring on a large timescale and has, for instance, provided direct experimental evidence about the fundamentals of proton diffusive motions in the water cage framework [DES 04, DES 12, DES 13, BED 14]. This aspect will be detailed in section 1.7 dedicated to ionic clathrate hydrates.

The dynamics of the guest molecules encapsulated within water cages is triggered by the cage potential energy surface, i.e. the host–guest interactions. It follows that accessing the cage energy landscape could be done through the analysis of the guest molecules dynamics, i.e. through the analysis of guest Brownian dynamics. The combination of incoherent QENS experiments and MD simulations yields a comprehensive model of the dynamics of guest molecules encapsulated in the cages of clathrate hydrate (e.g. [PEF 10, DES 11]). In a QENS experiment, clathrate hydrates are prepared with a deuterated host lattice so that only the guest molecules contribute to the incoherent scattering. The MD simulations box generally consists of a supercell (composed of several elementary unit cells) and MD simulations are run over several nanoseconds. The MD atomic trajectories can be used to calculate the incoherent neutron scattering laws within the same experimental conditions (i.e. by folding the MD-derived scattering laws with the experimental energy resolution function). Comparison of the MD-derived scattering laws with the experimental ones may lead to the “experimental” validation of the
MD simulations as soon as a correct agreement is observed (see example of the CH$_3$I-17D$_2$O s-II clathrate hydrate in Figure 1.6). The MD trajectories can then be safely analyzed to disentangle the various dynamical processes met in the clathrate hydrates [DES 11]. In a given type of cage, guest reorientations are generally modeled with a quasi-isotropic model: the guest molecule can adopt all orientations within the cage and preferred orientations may be adopted in the case of polar molecules [DES 11] or in the case of host–guest H-bonding [BUC 09, PEF 10]. The preferred orientations adopted by the guest molecules are different from cage to cage, in agreement with the disorder existing in the distribution of the water hydrogen bonding in the host network. This various local environment leads to a distribution of anisotropic energy landscapes (showed by the quasi-isotropic reorientations) experienced by the guest molecules. Despite these various local environments, no distribution of characteristic times is observed by means of MD-QENS investigation [DES 11].

**Figure 1.6.** Experimental QENS scattering laws (circles) and MD-derived scattering laws (continuous lines) of the methyl-iodide clathrate hydrate (s-II structure with only the large cage filled with guest molecules). The dashed lines represent inelastic contribution of the host cages (from [DES 11])
Finally, the main difference in terms of guest molecule relaxation times is observed for guest molecules occupying different types of cages. In other words, the relaxation characteristic time depends on the type of cages occupied by the guest molecule. This confinement differentiation is experimentally observed by means of QENS in the case of the bromomethane clathrate hydrates (s-I structure with both types of cage filled) [PEF 16]. As shown in Figure 1.7, the bromomethane molecule reorientations occur on a longer timescale in small cage than in large cage. This difference is a direct signature of the host–guest interactions, which are more attractive in the small cage than in the large cage [SCH 03]. Such a signature is similar to that observed in the vibrational spectra of methane clathrate hydrate [SUM 97]: the C–H stretching mode of methane confined in large cage is observed at higher frequencies than the one of methane confined in small cage.

![Figure 1.7. Experimental (points) and fitted (continuous lines) QENS spectra of CH$_3$Br–5.75D$_2$O at 50 K for various values of Q. The continuous lines represent the fitted scattering laws and the dashed lines represent the two QENS components. The broader component is associated with the guest molecules located within large cage. Instrument: NEAT at HMI, Q = 2.1 Å$^{-1}$, $\lambda_0 = 5.1$ Å, $\delta E = 100$ μeV. Adapted from [PEF 16]](image)

1.3.3. **Excitations and vibrational density of states**

In addition to neutron scattering, Raman scattering or infrared absorption leads to detailed information about the intramolecular vibration modes (i.e. for energy excitations typically greater than 10 meV) (see Chapter 2). The specificity of inelastic incoherent neutron scattering (IINS) with respect to optical spectroscopy probably resides in the investigation of the low frequencies modes met in clathrates hydrates (wavelength and energy of neutron beams are in the range of these excitations). The crucial role played by the knowledge of low frequencies modes is
certainly typified by the anomalous behavior of heat transport properties in clathrate hydrates [STO 79, ROS 81, HAN 87, TSE 88, TSE 01, TSE 05]. Moreover, IINS is a highly selective probe for investigating the properties of hydrogen atoms from molecules confined inside the clathrate nanometric cavities. In the case of a relevant concentration of protons, the bands in the spectra due to the host vibrational modes not involving hydrogen are typically quite weak. Another unique feature of IINS is the sensitivity of neutrons to rotational transitions, which are not probed in optical, infrared and Raman spectroscopies. Those transitions involving the conversion from ortho-hydrogen to para-hydrogen and vice versa have been extensively studied, in particular in the context of investigations about hydrogen adsorption in hydrogen storage materials (see section 1.4.3).

Figure 1.8. Inelastic neutron scattering spectrum of the iodomethane clathrate hydrate CH₃I·17D₂O at 1.8 K (NEAT time-of-flight spectrometer @HZB-Berlin with λ₀ = 7.0 Å, ΔE = 50 μeV and <Q> = 1.6 Å⁻¹). Points are experimental data and continuous lines are resulting from the fit of three tunneling transitions. Adapted from [PRA 04b]. For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip

The dynamical properties of s-I methane hydrate have been the subject of numerous works, including MD simulations [GUT 01, ENG 03, SUS 08], and inelastic neutron scattering [TSE 97], inelastic X-ray scattering [BAU 03] and NMR [RIP 88, RIP 04] experiments. Almost free rotation and very anharmonic low-frequency translation (the so-called rattling mode) are observed. The quantitative analysis of the MD at the lowest temperature shows a single-particle quantum rotation in weak rotational potentials differing slightly from cage to cage. This static distribution of the local environment owes to different arrangements of the H bonds in the cage surface [GUT 01]. Details about these various H bonds arrangements have been obtained by analyzing the dynamics of simple model systems of polar guest molecules: high-energy resolution QENS experiments have thus been
performed to analyze the rotational tunneling of guest methyl group in the series of methyl halide clathrate hydrates at low temperatures. Investigations have also been performed into the s-I clathrate hydrates (CH$_3$X–5.75 H$_2$O with X = F, Cl and Br) formed with fluoromethane [PRA 05], chloromethane [PRA 08] and bromomethane [PRA 07]. Despite the 1-D character of the methyl-halide rotor, complex tunneling spectra are observed due to the distribution of potential energy barriers as observed in the case of the 3-D methane rotor. The iodomethane clathrate hydrate crystallizes in the type II structure with only large cages filled. This “simplification” provides a unique opportunity to explore the nature of the inhomogeneity of potential energy barriers [PRA 04a, PRA 04b]. The neutron scattering spectrum of the iodomethane clathrate hydrate, CH$_3$I•17D$_2$O (Figure 1.8) is constituted of three broad inelastic peaks, corresponding to three tunneling transitions. While the broadening can be explained by different distribution of the H-bonds between water molecules (inducing slightly different potentials from cage to cage), the existence of three tunneling transitions is surprising since all iodomethane molecules are crystallographically equivalent (they are all located in 51264 cages). These peaks are in fact the experimental evidence of three types of adsorption sites existing at the cage surface [PRA 04b].

Large single crystals are generally required for neutron scattering experiments, but obtaining them is a tricky task. Consequently, vibrational densities of states (denoted VDOS) are often recorded on powdered clathrate hydrates to enable the study of their excitations. Such a projection of the lattice modes on the energy transfer axis leads to the loss of the dispersion information. Various options are then offered to interpret the data: use of isotopic substitutions (mainly, deuteration of selected chemical species), use of chemical substitutions (changing the guest molecules) or use of computing science (numerical modeling of the spectra). Examples of inelastic neutron scattering VDOS are shown in Figure 1.9. The translational modes at 7 and 10.5 meV are due to the host substructure [TSE 01]. The specific excitations (rattling modes) arising from the encapsulated guest are observed below 5 meV. The guest signature is not observed in the case of the argon clathrate hydrate because of the negligible scattering cross-section of argon, 0.7 barn, to be compared with that of oxygen (4.2 barn) or nitrogen (11.5 barn). This feature allows the extraction of the O$_2$ or N$_2$ contribution by differentiating their DOS with that of argon clathrate hydrate (Figure 1.9). Such spectra are composed of two bands attributed to the encapsulation in the two types of cage existing in the s-II clathrate hydrate. MD simulations [SCH 03] confirm this attribution. Additional information is provided by the MD analysis: the guest molecules encapsulated in the large cages exhibit a rattling mode with frequencies lower than the one in the small cages. As in the case of intramolecular vibrations or Brownian motions, these low-frequency signatures underline the importance of host–guest interactions in clathrate hydrates.
1.4. Selected examples

1.4.1. Inhibition and formation mechanisms

The blocking of pipelines by gas hydrate plugs is a source of concern for the oil and gas industry, especially the offshore industry where the conditions for natural gas hydrate formation are met (e.g. [SLO 10]). This industry devotes large capital and financial resources to prevention or remediation strategies by using pipeline insulation or heating and/or the injection of inhibitors. This obviously requires the understanding of fundamental properties of clathrate hydrates, such as thermodynamic stability, formation kinetics and growth mechanisms. This section focuses on the invaluable information provided by NPD.

1.4.1.1. Thermodynamic inhibition of hydrate formation

Salts such as NaCl are thermodynamic hydrate inhibitors: in comparison to pure water, higher pressures and/or lower temperatures are required to form methane clathrate hydrates in brine (Figure 1.10). As other examples, dimethylamine (DMA) or ethylamine (EA) also act as inhibitors of CH$_4$ hydrate formation [YOU 14]. Although these two compounds form type I pure clathrate hydrates, the inclusion of methane molecules as secondary guests under external gaseous CH$_4$ induces a structural transition into the type II phase. NPD experiments on the mixed methane/EA or DMA clathrates from 10 to 220 K show a significant and irreversible structure transformation at about 200 K. The clathrate structure evolves from a low temperature type II structure to a type I structure (Figure 1.11), an effect attributed...
to the release of methane just above 190 K, a temperature significantly lower than the usual methane hydrate temperature of dissociation. The P-T phase equilibrium data show that the inhibition effect increases with the increase in DMA or EA mole fraction [YOU 14].

**Figure 1.10.** Phase diagrams of the CH$_4$-H$_2$O clathrate hydrates systems. H, I, L$_W$ and V represent hydrate, ice, liquid water and vapor phase, respectively. The continuous and dashed-dotted lines show equilibrium pressures of hydrates formation for pure water and for 3.5 wt% NaCl systems, respectively. The dashed and two dashed-dotted lines show melting points of pure water and estimated geotherm in permafrost [KID 09, POH 09] (from [KOM 13]). For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip

**Figure 1.11.** Temperature dependence of the NPD patterns of the hydrate obtained from an EA (x = 0.0286) + D$_2$O + CD$_4$ mixture by increasing the temperature from 10 to 220 K followed by decreasing it to 20 K again. The black and light-gray patterns correspond to the s-II and s-I hydrates, respectively; *hexagonal ice; †s-I hydrate; ‡s-II hydrate (from [YOU 14])
Because of the transparency of high-pressure and cryogenic devices to a neutron beam, NPD represents a useful tool to follow the structural changes that occur under various conditions. This technique has enabled some successes in studying the clathrate hydrate kinetics of both formation and decomposition [STA 03, MUR 09, KUH 06a].

1.4.1.2. Formation kinetics

Gas hydrate formation from fluid (aqueous- and guest-rich) phases is a relatively slow process, and a large specific surface area is needed to reach conceivable growth rates in laboratory conditions. However, it has been proved that clathrates can be grown quickly from ice powders. For instance, the formation of deuterium clathrate from ice powder was found to be faster from powdered ice (~10 min) than from water (full conversion not reached yet after 5 days) [LOK 04, LOK 06]. The kinetics of clathrate formation from ice has mostly been studied in the case of methane or carbon dioxide clathrate hydrate. As observed in Figure 1.12, under constant pressure, both CO\textsubscript{2} and CH\textsubscript{4} clathrate formation are temperature-dependent processes, which show a fast initial and then a smoothly decreasing rate [HEN 00, WAN 02]. Methane hydrate formation from ice at low temperature is a much slower process. However, nearly complete conversion from hexagonal ice to both s-I CO\textsubscript{2} and CH\textsubscript{4} hydrate can be reached by slowly increasing the temperature through the melting point of D\textsubscript{2}O ice. On the basis of visual observations, in ice grains, a shrinking core model can be postulated, which involve the diffusion of future guest molecules through an outer mantle of hydrate to react with the inner core of ice [STE 01, HWA 90]. This model [JAN 27] considers a sphere of solid phase A (with radius \( r \)) that reacts with a mobile phase B (gas, liquid or solid powder) to form a product layer that covers the sphere A as the reaction proceeds. After the exposure of the solid phase A to the mobile species B, an initial layer of product is assumed to be rapidly formed, which may take a measurable amount of time \( t^{*} \). Then, once a product layer is formed on A after a time \( t^{*} \), the reaction is supposed to become diffusion controlled. The diffusion process of a particle from the outside during this diffusion-controlled stage can be described as follows:

\[
(1 - \alpha)^{1/3} = \left( -\left(\frac{2k}{r}\right)^{1/2} \right) \left( t - t^{*} \right)^{1/2} + (1 - \alpha^{*})^{1/3} \tag{1.29}
\]

where \( k \) is the diffusion constant, and \( \alpha \) and \( \alpha^{*} \) are degrees of reactions at time \( t \) and \( t^{*} \) (\(< t\)), respectively.

NPD data on formation reaction kinetics of carbon dioxide [HEN 00] and methane [WAN 02] clathrates were both successfully analyzed using this shrinking core model. In the case of carbon dioxide, results confirm that, after a time \( t^{*} \) corresponding to ~20% conversion, the rate limiting step of the formation process is the diffusion of CO\textsubscript{2} through the clathrate hydrate layer, characterized by an activation energy of 27.2 kJ/mol [HEN 00]. The conversion of ice into carbon
dioxide hydrate was modeled as a two-stage process. First, an initial fast conversion stage occurs. Its rate-limiting step before a layer of hydrate covers the ice particles is the reaction of CO$_2$ with a quasi-liquid layer (QLL) [TAK 00], a thin mobile phase of water molecules with mobilities in between those of liquid water and crystalline ice [MIZ 87]. Then, a slower second stage takes place, which is controlled by the diffusion of the CO$_2$ molecules through the layers of hydrate covering the ice particles. As this CO$_2$ diffusion is characterized by an activation energy lower than the energy needed to break the hydrogen bonding in ice (53.1 kJ/mol [ITA 67]) but greater than that of 21 kJ/mol in liquid water [SLO 08], the formation of the hydrate after the diffusion through the hydrate layer is suggested to occur through a reaction of CO$_2$ with internal water molecules in the QLL rather than with ice.

Figure 1.12. Conversion of deuterated ice into (left) carbon dioxide hydrate at 62 bars (from [HEN 00]) and into (right) methane hydrate at ~70 bar (from [WAN 02]) at various temperatures indicated on the figure. Each data point represents the mole fraction of hydrate refined from a 15 min histogram

In contrast, the diffusion of methane through a clathrate hydrate layer becomes the rate limiting step of the process at ~10% conversion and was characterized by an activation energy of 61.5 kJ/mol [STE 01]. A more complex shrinking core model [REK 95] describing the clathrate formation by a first initial reaction of methane with the surface of ice particle, followed by the growth of hydrate layer and inner diffusion of methane gas. Finally, the reaction of methane gas with ice at the unreacted ice core was tested. However, if results support the previous conclusion, it does not lead to any improvement of the neutron data fit. Considering the 61.5 kJ/mol activation energy, smaller than what is required for the dissociation of methane hydrate (81.2 kJ/mol [CLA 01] but greater than results in the CO$_2$ hydrate system involving QLL (27.2 kJ/mol [HEN 00]) and also than the energy needed to break the hydrogen bonding both in ice (53.1 kJ/mol [ITA 67]) and in liquid water (21 kJ/mol [SLO 08]), free liquid water phase does not seem to be required for converting ice into methane hydrate. This hypothesis is supported by results from the monitoring with a neutron spectrometer of the conversion under non-isothermal condition. Indeed, ice, existing above its melting point, is consumed at the same, but
opposite, rate as the amount of hydrate increases (Figure 1.13). These results exhibit either the existence of superheated ice or a demonstration of the insulating properties of hydrate layer, which may keep the ice core cooler than the measured temperature of the sample container. As for carbon dioxide hydrate, a two-stage model thus describes the conversion of ice to methane hydrate. The reaction starts quickly at the nucleation stage, and then the hydrate propagates as a hydrate layer that covers the ice particle. Further reaction is limited by the growth of the hydrate layer and inward diffusion of methane molecules through the hydrate layer to the unreacted ice core. However, in contrast with carbon dioxide hydrate formation, the reaction does not seem to involve interactions with a free water phase.

![Figure 1.13. Conversion of deuterated ice to methane hydrate through temperature ramp at 103 bar. Vertical line is the melting point of deuterated ice (from [WAN 02])](image)

### 1.4.1.3. Clathrate formation from ice particles

In most ice into hydrate conversion kinetics studies at temperatures close to the ice point, a thin gas hydrate film was reported to rapidly spread over the ice surface at the initial stage [HEN 00, STA 03, GEN 04, WAN 02, KUH 06b]. After this initial nucleation and ice surface coating, the only way to continue the subsequent clathration is the transport of gas molecules through the formed hydrate layer to the ice–hydrate interface, and/or the transport of water molecules from the ice core to the outer hydrate–gas interface. Indeed, due to the lower water density in the hydrate frame, excess water molecules diffuse outward to the hydrate surface to react with the ambient gas, which induces an outward expansion of the clathrate hydrate shell during the growth process. This can be modeled by a shrinking core approach, assuming that the reaction starts at the surface and proceeds toward the center of the ice particle. However, these considerations are inferred from the study of crushed ice
particles, whose geometry is ill-defined. Moreover, particle size analysis is not taken into account, despite its crucial impact onto formation kinetics.

For instance, during CO$_2$ clathrate hydrate formation from small ice particles ($\sim 10^{-1}$ µm) below 200 K, hydrate growth does not start with hydrate shell formation [FAL 11]. As the initial hydrate film thickness exceeds the ice particle dimensions, the whole ice volume is already transformed at the initial stage without reaching the permeation-limited regime. CO$_2$ clathrate hydrate growth quickly consumes the ice grain on which the nucleation has occurred but does not spread to neighboring particles. The overall speed of transformation and the size of the hydrate formed thus depend on the initial ice particle size taking into account the particles’ internal discontinuities (cracks, structural defects, grain boundaries) susceptible to hinder the spreading of the clathrate hydrate. As each of these effective particles needs to experience a nucleation event before it can be converted to clathrate (due to the high activation energy of nucleation, the stochastic nature of the nucleation event and the low activation energy of growth), smaller frost particles will tend to transform more slowly. Larger particles with larger surface areas have a higher probability to experience a nucleation event on their surfaces and would then transform faster by the clathrate spreading growth. The reverse tendency will take place when ice particle size exceeds 20–30 µm, allowing for hydrate shell formation around the remaining ice core. At temperatures equal or lower than 200 K, the main limiting factor for forming CO$_2$ clathrates may thus be the geometry of the starting material as well as the stochastic nature of the nucleation process.

The standard shrinking core model has been modified, mainly to account for the essential outward growth of the transforming particles and necking between them and to specify the initial phase of the clathration reaction on the ice particle surface [RYU 09]. The conversion of individual ice particles into hydrates was thus described by a first ice-surface coating stage in which an initially patchy hydrate film nucleates on and spreads over the surface of much larger ice particles [KAS 08]. The hydrate shell’s further growth around each ice core and includes the clathration reaction itself at the inner ice–hydrate as well as the external gas–hydrate interfaces and gas/water mass transport through the hydrate layer. At temperatures between 185 and 272 K, a recent study [FAL 13] of CO$_2$ hydrate formation from well-defined spherical ice powders has convincingly shown that this process is limited by the CO$_2$ transport (diffusion) through the hydrate shells growing around the ice cores. The modified shrinking core model gives experimental access to the values of the CO$_2$ permeation coefficient D in bulk hydrate reported in Figure 1.14, from which different activation energies are found above ($\sim 46$ kJ/mol) and below 225 K ($\sim 19$ kJ/mol).

Guests’ migration in clathrate hydrate framework requires the opening of the lattice cages, which may be well described by a model of migrating water vacancies
[HAA 09]. Assuming that the transport of water molecules from the ice–gas interface to the particle surface is the hydrate formation limiting step, activation energy is expected to be in the 12 kJ/mol range characterizing the water permeation process [KOM 00]. On the other hand, activation energies for the creation of a water vacancy-interstitial pair in CO$_2$ hydrate and for molecular CO$_2$ transport in a cage-to-cage mechanism in presence of a water vacancy are estimated respectively as 39 ± 6 kJ/mol [MAT 11] and between 12.5 kJ/mol (large cage–large cage) and 25 kJ/mol (large cage–small cage) [HAA 09]. The experimental activation energies thus seem to be related to carbon dioxide jumps mediated by available extrinsic water vacancy defects below 225 K, while above 225 K the increased activation energy is either a consequence of the creation of vacancy-interstitial pairs or simply the result of jumps between defect-free cages, which must then be rate limiting due to the small number of extrinsic defects. Therefore, gas molecules can migrate through bulk hydrate via cage-to-cage hopping promoted by vacancies of water molecules in the connecting cage wall. The rate limiting process at temperatures below ∼225 K is the cage-to-cage jumping of CO$_2$ molecules via a “hole-in-the-cage” mechanism involving extrinsic water vacancies in cage walls, while at higher temperature the creation of water vacancy-interstitial pairs become the rate limiting process. These results seem to be generalized to the methane hydrate case at least at temperatures above 225 K. Indeed, the permeation coefficients for CH$_4$ molecules in the hydrate framework at temperatures above ∼225 K can be estimated by MD simulations assuming a water vacancy assisted mechanism for the cage-to-cage hopping [HAA 09]. As seen in Figure 1.14, even if the values are about three times smaller than those experimentally obtained of CO$_2$, activation energies are quite similar.

Figure 1.14. Apparent activation energies for carbon dioxide (red and blue) and methane (green) diffusing through clathrate hydrate lattice deduced from permeation coefficient (denoted D) measurements (from [FAL 13]). For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip
1.4.2. Guest replacement in gas hydrates

The large deposits of natural gas hydrate in deep oceans and permafrost have motivated a large research effort [SLO 03, CHA 05, KOH 07, SLO 08]. The amount of methane in these deposits, about 700,000 trillion cubic feet according to some authors [BOS 09], corresponds to an amount of carbon greater than that of all conventional fossil fuels on earth [HAQ 99, MAX 00, COL 02, DEM 10]. It may represent an enormous supply of energy reserve, and a future energy source if the gas can be recovered economically and safely. The recovery of methane from these resources has been extensively studied, leading to actual recovery tests [RYU 09, KID 09, POH 09, CRA 09, LIU 09]. Most recovery techniques involve the promotion of the methane clathrate dissociation by using external stimulation such as thermal treatment [CRA 09], depressurization [LIU 09] and inhibitor addition [DEM 10]. Furthermore, extracting methane from the hydrates and simultaneously replacing it by its greenhouse gas product, carbon dioxide, could be a two-in-one approach. This concept, referred to as CO₂–CH₄ replacement, is expected to present benefits for stabilizing the ocean floor and the permafrost zones during the recovery process [OHG 96, BRE 99, KOM 02, LEE 03, YOO 04, OTA 05, PAR 06, GRA 08]. This section is devoted to gas replacement in gas hydrates.

1.4.2.1. Thermodynamic and structural considerations

CH₄ and CO₂ clathrate hydrates both crystallize according to a cubic structure s-I, where the guest can be trapped in both small pentagonal dodecahedral (5₁₂) and large tetrakaidecahedral (5₁₂₂) cages [WAN 02, HEN 00]. Indeed, the ellipsoidal shape and size (~6.2 Å in including van der Waals interactions) of the large cavity allows the confinement of either the methane molecules or the linear carbon dioxide molecule (~5.12 Å long). The small, roughly spherical cavities easily trap the methane molecules and, even if not ideal for a linear guest molecule, provide a tight fit for CO₂ as its van der Waals diameter is roughly equal to the length of the carbon dioxide molecule (~5.12 Å long). The methodology of CO₂–CH₄ replacement consists of the injection of high pressure carbon dioxide below sea beds, where replacement of the methane by CO₂ is expected to occur, at least for pressures not exceeding 8 MPa (water depths < 800 m). Indeed, as observed in Figure 1.15 [WAN 02, KOM 13, GOE 06], CH₄ hydrate is less thermodynamically stable than CO₂ hydrate for such pressures or depths. Measurements of methane and carbon dioxide distribution coefficients between gas and hydrate phases also show that the second if preferred in the hydrate phase over methane [OHG 96]. Injection tests with mixtures of CO₂ and N₂ below sea beds were successfully conducted in 2012 by the DOE (Department of Energy, USA).
However, partial failures/slowness of this replacement processes may have drastic consequences, as methane is, for instance, a greenhouse gas 20 times more effective in causing global warming than carbon dioxide [HOU 96]. Furthermore, as gas hydrates stability is very sensitive to the gas ratio and the conditions of temperature and pressure, any changes of these factors may lead to regrowth processes and affect the cementing properties of gas hydrates in a sedimentary matrix. Considering such broad implications, a full understanding of the replacement process should be obtained to design safe, efficient and economically feasible large-scale recovery. Kinetic aspects of replacement reaction in clathrate hydrate especially required a particular attention, since results suggest that the replacement reaction could be possibly dominated by kinetics rather than equilibrium thermodynamics [LEE 04].

1.4.2.2. Kinetics of replacement processes

Although NPD is a reliable method for studying microscopic occupation by guest molecules, it has not been applied to CH₄–CO₂ replacement reactions yet and
Neutron scattering experiments have led to detailed analysis of the kinetics in the cases of CO₂/Argon and methane/ethane replacement reaction in clathrate hydrate [HAL 01, MUR 10]. A first interesting feature is that hydrate formation on an existing hydrate surface appears faster than the formation of new hydrate. This was assumed to be due to the fact that the initial hydrate can act as a template. Introduction of carbon dioxide molecules at a 62 bar pressure on the s-II Argon clathrate induces its conversion into a mixed Ar/CO₂ s-I clathrate hydrate [HAL 01]. The kinetic rate, in contrast to hydrate formation from ice, indicates that the whole conversion is diffusion-limited (Figure 1.16). The diffusion process is characterized by an activation energy of 58.2 kJ/mol, higher than what is needed to break hydrogen bonding in either water or ice. A study of the s-II Ar hydrate decomposition as a function of the type of gas used and its pressure has reveals that the decomposition is slower under pressure of a non-hydrate forming gas than under the same pressure of CO₂ [HAL 01]. Although the existence of an undetectable intermediate phase cannot entirely be excluded, these observations – the absence of ice peaks in the neutron scattering pattern and the empirical report of a whole conversion dominated by diffusion – suggest that the conversion does not require any intermediate phase with weaker hydrogen-bonding energies. The transformation of the s-II Ar hydrate to the mixed Ar/CO₂ type s-I hydrate was thus assumed to be a direct conversion mechanism without first decomposing into ice. This leads to envision gas hydrate as an equilibrium assemblage in which hydrogen bonds open and close constantly, allowing guest molecules to leave or enter freely during that time.
Similarly, exposing pure s-I ethane hydrate to free methane gas at 5 Mpa induces an instantaneous formation of mixed s-II hydrate. The formation rate is temperature dependent and shows a nonlinear fast formation followed by a slower diffusion limited growth of the new s-II phase (Figure 1.17) [MUR 10]. Analysis of conversion from crushed and consolidated s-II ethane hydrate indicates that the growth kinetics is highly influenced by the surface area of the starting material. In agreement with the process suggested for hydrate formation from ice powder, the gas replacement in methane/ethane clathrate hydrates has been assumed to be a regrowth process involving the nucleation of new crystallites at the surface of the parent C$_2$H$_6$ s-I hydrate with a progressively shrinking core of unreacted material. Thus, mixed s-II
CH₄-C₂H₆ hydrate growth occurs around a shrinking s-I ethane hydrate core. Once a mixed s-II hydrate forms as surface coverage, a (fictitious) spherical s-I ethane hydrate grain shrinks, and its radius decreases due to the inward growth of the s-II hydrate layer. The structural transformation takes place at the replacement front with a rearranged composition of the constituents, and the CH₄-C₂H₆ s-II hydrate layer acts as a diffusion barrier both for the in-bound CH₄ molecules moving toward the replacement front and the out-bound C₂H₆ molecules moving toward the gas phase.

1.4.3. Hydrogen: from its dynamics properties to its storage capabilities

As gas hydrates usually show features such as large heat of dissociation and phase change temperatures above the ice point, they are considered promising materials for energy storage due to numerous advantages including intrinsic safety, environmentally benign and quite low processing costs [CHA 05]. Some applications envision new technological opportunities for storage and transportation of natural gases [SLO 08] and, most notably, hydrogen [DYA 99, MAO 02, FLO 04, LEE 05, PEF 12, VEL 14]. Indeed, conventional methods of hydrogen gas storage include compression and liquefaction, which both involve safety risk or demand high energy [SCH 05]. Strategies thus explore the possibility of using solid clathrate hydrate as an environmentally benign as well as non-explosive medium to reversibly capture, concentrate, store and release hydrogen fuel [SUG 09]. All these strategies include concepts in which hydrogen would be stored in its molecular form, and ready for utilization just by depressurization or minimal thermal stimulation. Consequently, numerous studies have been dedicated to improving the stability and storage capacity at near-ambient conditions of hydrogen clathrate hydrate.

In addition to the opportunity for hydrogen storage offered by hydrogen clathrate hydrates, these systems exhibit original and fundamental physicochemical properties. The understanding of the microscopic mechanisms underlying the development of hydrogen storage capabilities requires the detailed knowledge of the dynamic properties of hydrogen clathrate hydrate. Moreover, the fundamental investigations of the inherent quantum mechanical behavior of H₂ molecules “isolated” within cages play a key role in fundamental science. All these applied and fundamental aspects will be detailed in this section.

1.4.3.1. Thermodynamics characteristics

Hydrogen clathrate hydrates crystallize according to the s-II cubic structure at pressures between 750 and 3,100 MPa at 295 K or temperature below 145 K at ambient pressure [MAO 02]. NP shows that a maximum of one hydrogen molecule can be trapped in the small cavity in the pure hydrogen hydrate [LOK 04]. Below 50 K, each large cage traps four guests arranged in a tetrahedral geometry with a 2.93 Å D₂–D₂ distance and, increasing the temperature, the occupancy of the large
Gas Hydrates 1

Cages gradually decrease from 4 below 70 K to 2 at 160 K. As pure hydrogen hydrate formation requires considerably high pressure at ambient temperature, the co-inclusion of another guest molecule in the hydrate cages is considered in order to significantly reduce the formation pressure. Tetrahydrofuran (THF), which crystallizes in a pure stoichiometric (THF-17H2O) s-II hydrate when a mix of 5.56 mol% THF with water is freezeed [HES 06], has been extensively studied [FLO 04, LEE 05, STR 06, AND 07, HAS 07, NAG 08, SUG 09]. Mixed s-II THF-H2 clathrate can be formed by applying a pressure of ~100 bar on a grounded THF clathrate hydrate. Phase diagrams for THF concentrations at boundary limits (i.e. 0 mol% THF corresponding to the pure hydrogen clathrate hydrate, 5.56 mol% THF corresponding to the s-II structure with the THF molecule filling all large cages and the hydrogen molecules located in the small cages) are shown in Figure 1.18. Others promoters of s-II mixed hydrogen clathrate hydrate have been identified (phase diagrams reported in [VEL 14]). Cyclopentane increases dissociation temperature compared to THF. Furan and tetrahydrothiophene lead to stabilization at lower temperature and faster absorption of hydrogen than THF systems for the same storage capacities under the tested experimental conditions [VEL 14]. Cyclohexanone (CH) has also been considered but, despite larger size hydrate cages (due to the size of CH), the mixed CH-H2 hydrate has lower hydrogen occupancy than that formed with THF as a promoter [VEL 14].

Apart from hydrogen storage in s-II clathrate hydrate (pure or mixed with promoters), it is possible to have hydrogen molecules occupy the cages of different hydrate structures that hydrogen cannot usually form. Inclusion of single or two hydrogen molecules in the small cages of s-I CO2 hydrate while the large ones are filled by CO2 has been reported [KUM 09]. The opportunity of storing hydrogen in both types of s-I cages has also been demonstrated by initially forming s-I hydrate (with CO2 or CH4 molecules as guest species) and then by pressurizing the system with hydrogen gas [GRI 12]. On the other hand, experimental storage of hydrogen along with a larger guest molecule has been in the small s-H cages [VEL 14]. Such storing opportunity leads to an increase in hydrogen storage capacity by 40% compared to binary hydrogen s-II hydrates [VEL 14]. However, the formation of such s-H hydrate requires extreme conditions: about 100 MPa pressure at 273 K. Such pressure prevents from considering practical applications despite its high storage abilities. Moreover, a distinct structure s-VI, which could be capable of storing maximum hydrogen compared to other hydrates due to the size of the cages, has also been recently reported [DU 11]. The mixed tert-butylamine/hydrogen hydrate can then be formed with stability at lower temperature than most of the mixed hydrogen hydrates formed with promoters. It is interesting to note that recent MD simulations outline the existence of interstitial site welcoming hydrogen molecules in between two cages [GRI 14]. Finally, semicladdrate hydrates made up of quaternary ammonium and phosphonium salts also host hydrogen (represented in Figure 1.19). In such cases, the formation conditions are relaxed to lower pressures.
and higher temperatures (i.e. closer to room temperature condition) as shown in Figure 1.19 [CHA 07].

**Figure 1.18.** Phase equilibrium data for hydrogen clathrate hydrate (opened circles), THF clathrate hydrate (filled diamonds) and THF-H\textsubscript{2} clathrate hydrate (with 5.56 mol\% THF in water; filled circles and crosses). Varying the concentration of THF between 0 and 5.56 mol\% in water leads to equilibrium curves of the formed THF-H\textsubscript{2} clathrate hydrate contains in between the equilibrium curves of the pure hydrogen clathrate hydrate and the “THF + H\textsubscript{2}” clathrate hydrate [VEL 14]. Adapted from [FLO 04, PEF 12]. For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip

**Figure 1.19.** Phase equilibrium data for mixed hydrogen hydrate formed with various semiclathrate promoters. TBAB: tetrabutylammonium bromide. TBAF: tetrabutylammonium fluoride. Adapted from [CHA 07]. For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip
1.4.3.2. Cage occupancy

Guest occupancy is an essential factor for storage in clathrate hydrates. It varies with temperature and pressure, the use or lack of additives, and is mainly dominated by adsorption–desorption equilibrium. The guest occupancy of hydrogen clathrate hydrates takes a particular importance in the case of mixed hydrogen hydrates. Indeed, even if the use of promoters enhances the hydrate formation it also reduces the storage ability. When mixed hydrogen hydrates form in the presence of a promoter, the promoter molecule preferably occupies large cages stabilizing the hydrate structure thereby making it difficult for hydrogen molecules to enter and occupy the large cages. However, at certain low concentrations of promoter, hydrogen molecules have been reported to partially occupy the large cages, thus increasing the hydrogen content [LEE 05, KUM 09]. This phenomenon, referred as the “tuning effect” since the concentration of the promoter is tuned to achieve the maximum hydrogen storage, has first been reported in mixed THF/hydrogen hydrates. A maximum amount of hydrogen of 4.03 wt% was observed by lowering the concentration of THF from stoechiometric composition (5.56 mol%) to 0.15 mol% at 12 MPa [LEE 05]. Data about hydrogen storage capacity as a function of THF concentration compiled from literature data are presented in Figure 1.20. Even if such a tuning effect has also been reported in mixed hydrogen hydrates with
various promoters (see various examples in [VEL 14]), the guest occupancy of hydrogen clathrate hydrate remains a conflicting subject [LEE 05, MUL 08, KUM 09, PEF 12, VEL 14].

First, most of the studies reporting such a tuning effect used Raman spectroscopy, for which quantitative measurements of hydrogen content in gas hydrates are known to be a tricky task [STR 09]. Besides, other studies categorically refute the possibility of any tuning effect [HES 06, STR 06, HAS 07, AND 07, MUL 08] and report only a maximum of around 1 wt% corresponding to hydrogen stored in small cages [STR 06, AND 07]. For instance, the direct determination by neutron scattering of hydrogen occupancy in the small cavities of the binary deuterated hydrogen/THF hydrate provides evidence that only single occupancy of hydrogen in the small cavity can be expected in this system, at least up to 70 MPa [HES 06]. Neutron scattering is especially suited for the determination of the position and quantity of hydrogen (deuterium) and for clarifying the difference in the thermal vibrations of the same kind of atoms at crystallographically distinct sites and, if full structural refinement is performed, locates the hydrogen atom positions with high precision [HES 06]. In addition, in the case of single crystals, it also allows the refinement of multiple cage occupancy and orientation ordering in the cages (with e.g. pure H2 hydrates [LOK 04], binary H2/THF hydrates [HES 06]). Further quantitative NP analysis shows that, instead of the observation of “tuning” of the THF concentration in favor of hydrogen uptake in the large cages, reducing the THF content of this clathrate below its stoichiometric 1:17 ratio leads to phase separation of the pure clathrate and liquid water, which becomes ice at lower temperatures [MUL 08]. Thus, the stabilization of the THF-depleted clathrate phase by D2 in the vacant large cages compensating for the lower THF concentration is not observed. This investigation also measured a hydrogen occupancy in the small cages of the clathrate (at pressures of up to 95 bar and $T = 264$ or 274 K) significantly smaller than expected, reaching only 30% at 274 K and 90.5 bar, which is equivalent to 0.27 wt% H2 storage. Any improvement in the hydrogen content requires further knowledge about the mechanisms of hydrogen loading in clathrate hydrate. In addition, such an approach may help to design a system that overcomes the typical limitations of kinetics, mass and heat transfer for the gas storage (natural gas or H2).

1.4.3.3. Mechanism of hydrogen loading in THF clathrate hydrate

The hydrogen loading mechanism in THF clathrate assumes hydrogen adsorption onto the clathrate particle surface and the subsequent diffusion of hydrogen into the clathrate hydrate particle. This diffusion is the process-limiting step and is characterized by a high activation energy of 78.7 kJ/mol [NAG 09]. The thermally assisted rapid diffusion of hydrogen has been observed during its loading in the mixed THF hydrogen clathrate [MUL 08] by means of in situ powder NP (Figure 1.21). At 264 and 274 K, the clathrate hydrate takes up hydrogen rapidly at pressures between 60 and 90 bar as D2 molecules rapidly diffuse through the THF
clathrate, with a diffusion coefficient estimated of at least $10^{-11}$ cm$^2$ s$^{-1}$ at 264 K. The diffusion slows down below 220 K, leading to the stagnation of further uptake at lower temperatures. The maximum hydrogen occupancy in the small cage of about 0.43 achieved at around 50 K is reduced by increasing temperature up to 220 K and progressively drops to zero when approaching 282 K. Subsequent application of high hydrogen pressure at 282 K reproduces a D$_2$ cage occupation of approximately 0.3. Diffusion of hydrogen through the crystalline clathrate is thus found to be fast enough to enable (un-)loading from the gas phase at temperatures down to about 220 K. Above this temperature, the clathrate behaves as a nanoporous material.

![Figure 1.21](image-url) **Figure 1.21.** Diffraction patterns as a function of the temperature for deuterated THF·17 D$_2$O + 0.07 D$_2$O. Ice Ih Bragg peaks are observed at 3.7 and 3.9 Å (below ca. 273 K) next to the TDF·17 D$_2$O clathrate peaks (TDF holds for deuterated THF). At the applied pressure (90 bar), the clathrate melting point is approximately 284 K, which is consistent with that given in [FLO 04]. Above the melting points of the crystalline phases, broad diffraction features corresponding to the liquids are visible (i.e. liquid D$_2$O between 284 and 274 K and a liquid mixture above 284 K) (from [MUL 08]). For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip

Considering the size of the pentagonal windows connecting the small cages (4.24 Å at 264 K) and taking van der Waals radii into account, the approximate window openings is ca.1.2 Å. Such a value is significantly narrower than the kinetic diameter of a hydrogen molecule (2.89 Å). The potential energy barrier associated with H2 guest molecules migration through hexagonal face of the large cage and smaller pentagonal faces of the small cages of the s-II clathrate hydrate are, respectively, estimated about 23 kJ/mol and between 104.7 and 121.4 kJ/mol (depending on the orientation of the H2 molecule) [ALA 07]. As for CO2 diffusion during ice to CO2 hydrate conversion, hydrogen molecular transport is thus facilitated by (transient) defects in the structure, leading to a temporary opening of
the cage window. Diffusion of $D^+$ ions in THF clathrate lattice results from the combination of deuteron translational diffusion (deuteron exchange between two O atoms involving OD$^-$ and/or D$_3$O$^+$) with a correlation time around 264 K of about $10^{-3}$ s, and Bjerrum defects mobility (reorientation of an O–D bond) up to two orders of magnitude faster [KIR 03]. Assuming that the timescale of the molecular transfer of $D_2$ from a small cage to another is related to the passage of defects, its diffusion coefficient will thus be between $10^{-12}$ and $10^{-10}$ cm$^2$/s, depending on which type of defects dominates. The magnitude of the above-estimated experimental lower limit for the $D_2$ diffusion constant is inbetween these two extremes [MUL 08].

Besides, the hypothesis assuming that Bjerrum and ionic defects facilitate $D_2$ diffusion could also explain the observed slowdown of hydrogen uptake and release at lower temperatures by the strong temperature dependence of the occurrence of such defects (as reported in [KIR 03]). In this respect, the clathrate behaves very differently from other surface-adsorption materials, because the diffusion pathways between the available adsorption sites are progressively obstructed upon reducing the temperature. Furthermore, as the transport of hydrogen molecules between the cages may only proceed in the neighborhood of a cage vacant guest site, the hydrogen diffusion coefficient value also gradually decreases with increasing pressure or increasing hydrogen concentration in the hydrate [STR 06].

1.4.3.4. Hydrogen dynamics in mixed THF/H$_2$ clathrate hydrates

At room temperature, free hydrogen molecules consist of two different species (namely ortho and para) separated by an unperturbed energy difference of 14.7 meV. The ortho population is almost three times that of para at room temperature but, upon cooling, the lower energy para-population increases because of an ortho- to para-transition induced by the strong magnetic field generated by a neighboring H$_2$ molecule. When a hydrogen molecule is incorporated into a hydrate cavity, its chemical environment adds a potential barrier to the rotational motion of the molecule, which usually results in a decrease of the ortho- to para-transition energy. IINS is especially sensitive to this transition (Figure 1.22). IINS experiments have led to a detailed analysis of rattling modes of the hydrogen molecule inside the small cage of mixed THF/H$_2$ [ULI 07, XU 08, CHO 10, XU 11, COL 13]. At 2 K, a single peak at about 13.6 meV is observed and, increasing the temperature above 10 K, a second peak appears at 14.7 meV in addition. The small shift between the peaks suggests that, even if the trapped hydrogen molecules are still relatively free from their host at 2 K, a rotational barrier certainly exists [CHO 10]. Finally, at 20 K, a threefold splitting of both the para- to ortho-transition attributed to the anisotropic structure of the cage was reported at 13.64, 14.44 and 15.14 meV [ULI 08]. Both H$_2$ roton and vibron bands are at lower frequencies in clathrate cage structure than in the free gaseous phase [FLO 04, ULI 07, TAI 07, ULI 08, CHO 10], which is representative of the attractive interaction existing between the H$_2$ molecule and the aqueous cage.
Figure 1.22. The clathrate IINS spectrum (thick blue line) decomposed into the sum of the ortho-H$_2$ (black, solid) and para-H$_2$ (red, dashed) contributions. The para-H$_2$ spectrum exhibits the strong $J = 0 \rightarrow 1$ rotational band (a triplet at $E \sim 14$ meV), and the ortho-H$_2$ spectrum exhibits the splitted band around 10 meV, due to the quantum rattling motion of the molecule in the cage. Adapted from [ULI 07]. For a color version of this figure, see www.iste.co.uk/broseta/hydrates1.zip

In general, the molecules enclosed within the cages of mixed hydrogen clathrate hydrates are trapped because the small hexagonal and pentagonal windows make transport between the cages impossible. However, from structural point of view, hydrogen molecules could be assumed to occasionally jump from one small cage to an unoccupied neighboring small cage, as observed during the microscopic hydrogen loading or unloading process in THF clathrate. At low temperatures, hydrogen molecules are not energetic enough to penetrate the potential barrier between the small cages but at high enough temperatures the occurrence of such a process could be observed in neutron scattering spectra. While only a slight increase in the signal of IINS spectra of mixed THF/H$_2$ clathrate hydrate is observed up to 60 K, this signal shows a sudden jump between 60 and 65 K, which persists at higher temperatures [CHO 10]. As this strong signal jump is attributed neither to macroscopic unloading of hydrogen at 120 K nor to any structural change, it strongly suggests hydrogen molecular diffusion in the crystalline lattice. QENS spectra on a picosecond timescale above 100 K confirm the observation of diffusive motions of the hydrogen molecules (Figure 1.23) [PEF 12]. However, these H$_2$
molecular translations, characterized by a low activation energy of $1.59 \pm 0.06$ kJ/mol, are found to occur within localized spherical area of the small s-II cage: the dynamical diameter of volume visited by the H$_2$ molecules varies from 2.08 Å at 250 K to 1.64 Å at 100 K and the diffusion constant ranges from $0.16 \pm 0.03$ rad ps$^{-1}$ at 100 K to $0.49 \pm 0.03$ rad ps$^{-1}$ at 250 K [PEF 12]. No diffusion between the cages is observed in the picosecond time scale [PEF 12, CHO 10, TAI 07]. Regardless of temperature and pressure, the atomic displacement factor for the D atom of the D$_2$ molecule in the small cages is about 0.17 Å according to NP. Such a value is close to what may be expected for a tumbling D$_2$ molecule that cannot leave the small cage on the picosecond timescale [MUL 08], in agreement with the QENS analysis [PEF 12].

![Figure 1.23. Quasi-elastic neutron scattering (QENS) spectrum of the H$_2$-TDF-17D$_2$O (TDF stays for deuterated THF) at Q = 1.8 Å$^{-1}$. The dotted line represents the QENS signal of H$_2$ confined into the small cage of the s-II clathrate hydrate. The dotted line represents the QENS contribution arising from the deuterated storing clathrate hydrate TDF-17D$_2$O. The elastic line is a direct signature of the non-existence of intercage H$_2$ diffusion. NEAT @HZB (Berlin, Germany), $\Delta E \approx 100 \mu$eV, $\lambda_0 = 5$ Å. Adapted from [PEF 12].](image)

1.4.4. Ionic clathrate hydrates and semiclathrates

Another research area focuses on the specific properties met in the case of ionic clathrate hydrates. In such systems, the ionicity originates from the incorporation of ionic species mainly as guest molecules. The inclusion of ionic guest molecules
The incorporation of counter-ions within the water framework. Such chemical defects – leading to the violation of the ice rule – induce modification of the intrinsic properties of the clathrate hydrates. Their structural properties exhibit a large variability ranging from a semiclathrate structure of quaternary ammonium salts [SLO 08] to a rich structural phase diagram depending on the hydration number as in the case of strong acids [BOD 55, MOO 87, CHA 08]. The thermodynamics of gas hydrates, such as their heat capacities, is modified by the addition of ionic species such as KOH [YAM 88] or ammonium salts [SAN 14]. Among the fascinating properties of ionic clathrate hydrates made with alkyl ammonium hydroxide [BOR 96, OPA 95, CAP 94] or strong acids [CHA 08, HUA 88, ASC 94], their superprotonic conductivity is due to a supermobility of protons in the host substructure [DES 04, DES 13, BED 14]. The supermobility of protons in the host substructure [DES 04, DES 13, BED 14]. The modification of proton dynamics promoted by the addition of ionic species in the host substructure may also switch the thermal conductivity from an abnormal “glass-like” behavior to a standard crystalline behavior [KRI 08]. Recently, it has been shown that the substitution of few THF molecules by strong acid molecules within the s-II THF clathrate hydrate modifies the thermodynamics and the cage flexibility of the clathrate hydrate [DES 15]. Finally, unusual properties of ionic clathrate hydrates also include their superoxide ion formation [CHA 10], superexchange-like interaction [SHI 11a] or abnormal positioning of host molecules [SHI 14].

Finally, due to the ionic interactions between host and guest molecules, ionic clathrate hydrates exhibit many original physicochemical properties. These unique features make them particularly promising in various practical application fields such as solid electrolytes, gas sensors and gas storage. This section will address two specific properties linked to ionic clathrate hydrates and for which neutron scattering provides invaluable information: the potentiality for storing gaseous species as mainly investigated by means of NP and the microscopic mechanism of superprotonic conductivity as revealed by means of QENS.

1.4.4.1. Small molecule storage in semiclathrates

The development of fast and reversible methods for storing gas is of utmost importance (e.g. hydrogen storage [VEL 14], carbon dioxide capture and separation [YAN 08]). New alternatives propose improved gas encapsulation capacities in clathrate hydrate by storing the gaseous molecules both inside the clathrate cavities and as molecular species participating to the host lattice. Semiclathrates formed with quaternary ammonium salts are good candidates for that purpose. Semiclathrates are named from the fact that, while the cationic part of these typically ionic compounds occupies the cages of hydrate structure like a guest molecule, its anionic part is
involved in the lattice formation along with water molecules. These compounds have been extensively investigated as promoters for gas storage because of their improved stability and ease of hydrate formation close to room temperature and pressure compared to s-I and s-II hydrates (Figure 1.12).

In the particular case of hydrogen storage, semiclathrate hydrates such as tetrabutyl ammonium borohydride (TBABh) semiclathrate has been reported as a very promising hybrid material [SHI 09]. The improved storage capacities also arise from both guest-based and host-based atomic hydrogen generation [KOH 12]. The phase equilibrium data from the literature of mixed hydrogen clathrate with tetrabutyl phosphonium bromine, trimethyl amine (TMA) or tetrabutyl ammonium bromide (TBAB), fluoride (TBAF), chloride (TBAC) and nitrate (TBAN) are reported in the Figure 1.24 [VEL 14]. As revealed by this figure, the hydrogen/TBAF mixed hydrate appears to be the most stable hydrate formed at room temperature. However, as for the other mixed hydrogen clathrate formed with semiclathrate promoters, the storage capacity of hydrogen is less than that of hydrogen/THF mixed hydrates [VEL 14]: the maximum hydrogen storage capacity reported so far for the semiclathrate is in TBABh (0.5 wt%).

![Figure 1.24](https://www.iste.co.uk/brose/hydrates1.zip)

**Figure 1.24.** Phase equilibrium data for mixed hydrogen hydrates formed in the case of various semiclathrate promoters at different concentration (from [VEL 14]). For a color version of this figure, see www.iste.co.uk/brose/t/134/14015845.zip

The inclusion of small molecules such as H₂, D₂, N₂, O₂ or CH₄ as secondary guests has been investigated in tetramethylammonium hydroxide (TMAO) and
perchloric acid clathrates hydrates by means of powder NP [SHI 11b]. TMAOD (deuterated TMAOH) can form several clathrate structures but the inclusion of small non-ionic guest molecules in TMAOD–16D₂O induces its transformation in the s-II structure in which small gas molecules occupy the small cages and TMA cations are inserted inside large cages with the corresponding hydroxide group incorporated in the host lattice [SHI 08, CHA 10]. DCIO₄–5.5D₂O usually crystallizes within the s-I structure [MOO 87]: the acidic excess protons are delocalized on the host lattice and the DCIO₄⁻ anions occupy both cavities. Moreover, small non-ionic guest molecules can be included in the small cages over the anions under favorable host–guest interactions. Neither the basic s-II clathrate nor the acid s-I clathrate is profoundly affected by the size and mass of the secondary guest [SHI 11b]. The lattice expansion of binary s-II TMAOD hydrates clearly seems dominantly affected by the charge interaction between the lattice hydroxide ions and the secondary guest, especially in the presence of electronegative O₂ guests. Furthermore, the thermal expansivity of the mixed perchloric acid clathrate hydrates is considerably higher than that measured for non-ionic s-I hydrates. This may be explained by partial incorporation of ClO₄⁻ oxygen atoms in the host framework (through the occupation of host water vacancies [MOO 87, SHI 11a]), leading to an extraordinary host–guest interaction.

1.4.4.2. Superprotonic conductors

The superconductivity, the relatively soft formation conditions and the high melting temperature of ionic clathrate hydrates render these compounds promising as solid proton conductor materials. In acidic clathrate hydrates, the high conductivity is associated with the delocalization of the acidic proton in the cage structure, thus formed by hydronium ions in addition to the water molecules. Such ionic defects induce the violation of the ice rule and are dynamically delocalized. This proton diffusion is observed within the host lattice framework.

As detailed previously in sections 1.3.2 and 1.4.3.4, QENS is the appropriate technique to access displacements of hydrogen nuclei with spatial and time resolution. Using the time-filtering property of the instrumental resolution, QENS have thus enabled the disentangling of the host molecule dynamics in the HClO₄ and HPF₆ acid clathrate hydrates. Such investigations provide a comprehensive model for proton diffusion in ionic clathrate [DES 04, DES 13, BED 14].

While perchloric acid clathrate adopts the s-I structure [MOO 87], the hexafluorophosphoric acid clathrate hydrate crystallizes either in the s-I structure or in the type VII cubic structure (denoted s-VII), depending on the hydration number (typically varying between 4 and 7.67 H₂O molecules per HPF₆ acidic molecules).
The s-VII unit cell (space group \textit{Im3m} with \(\approx 7.7\text{Å}\)) contains 24 water molecules forming one single \(4^6\text{O}^8\) type of cages, all occupied by \(\text{PF}_6^–\) ions, leading to a ratio of six water molecules per \(\text{HPF}_6\) molecules [BOD 55]. A structural phase transition between s-I and s-VII structures is observed at ca. 230 K for hydration numbers greater than 6 [CHA 08, BED 14].

Proton diffusion in s-I \(\text{HClO}_4–5.5\text{H}_2\text{O}\) clathrate has been characterized by a diffusion coefficient reaching \(3.5 \times 10^{-8}\) cm\(^2\)/s at 220 K and an activation energy of about 0.3 eV [DES 04]. In the s-I phase of the \(\text{HPF}_6\) clathrate hydrate (i.e. at temperatures lower than 230 K for the studied sample), the diffusion coefficient of protons was found smaller than ca. \(10^{-7}\) cm\(^2\)/s [BED 14], which is in agreement with results in the perchloric acid clathrate hydrate adopting the same structure. In contrast, in the s-VII phase of \(\text{HPF}_6\) clathrate hydrate (i.e. between ca. 230 K and room temperature), the long-range proton diffusion coefficient was measured up to \(3.85 \times 10^{-6}\) cm\(^2\)·s\(^{-1}\) at 275 K, with an activation energy of about 0.19 eV. To our knowledge, such diffusion coefficients appear to be one of the most important ones measured so far in ionic clathrate hydrates.

For both clathrate hydrates, excellent agreement between data from proton pulse field gradient NMR (\(^1\text{H PFG NMR}\)) and QENS experiments (which characterize proton diffusion at long distance and at a molecular scale, respectively) lead the representation of long-range proton diffusion microscopic mechanism with the help of the Chudley–Elliot jump diffusion model [DES 04, BED 14], indicating that the proton jump occurs between host oxygen sites. On a molecular scale, the proton diffusion coefficient has indeed been characterized by its mean residence time and its mean jump distance, because of the momentum transfer sensitivity of QENS technique. The mean jump distance was measured as 2.8 and 2.79 Å for \(\text{HClO}_4\) and \(\text{HPF}_6\) acid clathrate, respectively. Such values match the O–O distance of water cages. The mean residence time of protons on each crystallographic site was determined as 3.7 ns at 220 K for the perchloric acid case. In the \(\text{HPF}_6\) case, the higher proton conductivity is related to significantly shorter mean residence times: 0.2, 0.052 and 0.03 ns at 230, 255 and 280 K, respectively.

From these results, the superconductivity of acidic clathrate hydrates, attributed to proton diffusion along the clathrate aqueous framework, appears to result from a series of protons jumps from one to another oxygen, which is in good agreement with the Grotthuss mechanism. Grotthuss mechanism assumes that protons are transferred along hydrogen bonds from one water molecule of the host framework to another with the assistance of the reorganization of this diffusing proton environment, including lattice molecule reorientation. According to this mechanism, several localized dynamical processes occurring on a broad timescale
are thus involved. In the HPF$_6$ acid clathrate, the mean time associated with these localized dynamical processes has been measured as 2.5 ps at 255 K with an activation energy of 0.24 ± 0.04 eV [BED 14]. Localized diffusive motions of the proton surrounding the oxygen sites thus occur more frequently than the proton jumps between oxygen sites over a long-range. However, despite this timescale difference, the energy barrier associated with the localized diffusive motions appears slightly higher than that of long-range diffusion (about 0.19 eV). The limiting step for the proton conductivity thus occurs on local spatial scale, which confirms the key role played by the surrounding of the acidic proton in the long-range proton diffusion.

QENS experiments performed by tuning the observation time to the timescale of the probed dynamical process met in the perchloric acid clathrate hydrate at 220 K have led to disentangle three different localized dynamical processes occurring on this clathrate lattice. First, water molecules reorientations are reproduced well by a model describing proton jumps between two sites separated by 1.45 Å on which the mean residence time is about 0.7 ns at 220 K [DES 04]. These motions are characterized by an activation energy of about 0.18 eV and can be considered as the limiting elementary step in the mechanism of the proton conductivity met in the perchloric acid clathrate hydrate. Then, two dynamic elementary processes are identified for the hydronium ions: hydronium reorientations coupled to intermolecular proton transfer [DES 13]. Hydronium ions of the clathrate lattice are found to undergo reorientations over four different orientations tetrahedrally distributed with a jump distance of about 1.31 Å and a characteristic time of about 42 ps at 220 K. The transfer of a hydronium proton within the hydrogen bridge formed between a “hydronium” oxygen site and a neighboring “water” oxygen site is described by means of a jump model between two proton sites separated by about 0.96 Å and occurs with a characteristic time of about 1.4 ps at 220 K.

While this jump distance is in full agreement with the structure determination, the values obtained for both H$_2$O and H$_3$O$^+$ molecular reorientations appear shorter than the 1.6 Å value expected assuming a “standard” configuration of these molecules in the clathrate lattice [MOO 87]. This suggests that the oxygen atoms do not coincide with the center of rotation of the reorientation motions. Such an assumption is supported by results from X-ray diffraction analysis, which show large isotropic thermal parameters of cage atoms (values between 2.05 and 2.95 Å$^2$ for oxygen atoms and of 4 Å$^2$ for the protons) and indicate that the distribution of proton site around the oxygen atom is slightly distorted from perfect tetrahedra [MOO 87]. As shown in the examples reported in Figure 1.25, the complete model including components due to long range proton diffusion, to H$_2$O and H$_3$O$^+$ reorientational motions and to proton transfers through hydrogen bonds lead to an excellent reproduction of the perchloric acid clathrate QENS spectra whatever the observation times (energy resolution) and the momentum transfers are [DES 13].
Figure 1.25. Experimental (symbols) and fitted (thick continuous line) QENS spectra of perchloric acid clathrate at 220 K. QENS contributions due to water molecule reorientations and long-range proton diffusion are shown as thin continuous lines. The dotted line represents the contribution related to the lattice hydronium ions reorientation, the dashed line represents the contribution due to proton transfer within hydrogen bond and the dashed-dotted line stands for the contribution related to the coupling of these two phenomena (from [DES 13])

1.5. Concluding remarks

The array of investigations carried out on clathrate hydrates is probably a result of the peculiar implications in the broad field of energy, technology and
environment. Whatever the hydrate research area, a fundamental understanding of the microscopic mechanisms governing the properties specific to their cage structure constitutes the necessary basis for further developments. This chapter has reviewed the contribution of neutron scattering techniques to fundamental and applied issues. In addition to the description of the basics of neutron scattering, the invaluable information revealed by these techniques has been reviewed not only for structural aspects, but also for spectroscopic aspects, providing information ranging from Brownian relaxations to intramolecular vibrations. Detailed examples are treated, when possible, in conjunction with applications of gas hydrates, e.g. in the fields of energy recovery and hydrogen storage. The main information includes thermodynamic aspects (i.e. knowledge of phase boundaries and equilibrium guest compositions) and the kinetic features associated with the formation of clathrate hydrates, which play a role in the determination of limitations and of viable approaches for gas replacement (e.g. CO₂–CH₄) and in the design of systems overcoming typical limitations of kinetics, mass and heat transfer for gas storage. NP is particularly appropriate to structural investigations, but also to follow the structural changes that occur as a sample changes under “extreme” conditions (high pressure, low temperature). This technique has enabled some recent successes in studying the clathrate hydrate guest occupancy, kinetics of formation/decomposition, guest replacement reactions (especially when accompanied by a structural transition) and also provided useful information on the time dependency of hydrate transformations. Furthermore, inelastic neutron scattering provides information about excitations met in clathrate hydrates with the advantage of no application of selection rules unlike in optical spectroscopies (e.g. IR, Raman). It has allowed for a detailed description of gas adsorption at the cage surfaces and gas molecule dynamics in the clathrate hydrate cages. Finally, QENS provides access to relaxation processes; it has enabled us to disentangle the dynamics of clathrate hydrates occurring on a broad timescale and has for instance, provided direct experimental evidence about the fundamental aspect of inter- or intracage diffusion. In addition to “standard” properties accessed by means of neutron scattering techniques, such studies provide spectroscopic signatures of clathrate hydrates that might find numerous applications in astrophysics (hydrates might be involved in numerous models of planets and comets to geology (e.g. for in situ mapping of gas hydrates in deep ocean) and in various technological area (e.g. for improving the gas storage capacity in clathrate hydrates).

As detailed in this chapter, neutron spectroscopy techniques are very useful tools to serve various issues of “hydrate science” because of the striking features of the neutrons: they are neutral particles (matter is transparent to neutron), they interact with the nuclei rather than with the electronic cloud (neutron is sensitive to light element like hydrogen), they have (de Broglie) wavelength in the range of interatomic distances, their mass are in the atomic mass range and they carry similar energies and momentum than those of clathrate hydrates. From a methodological
point of view, the contribution of neutron scattering is significant and complementary to results obtained with other techniques such as X-ray scattering, Raman scattering or NMR. A powerful advantage of neutron scattering resides in the basic observable reached experimentally (via Fourier transforms): the time evolution of atomic positions. Such observable can be “easily” accessed with the help of numerical modeling by means of \textit{ab initio} or classical simulations. The possibility of comparing experimental and theoretical results, by using such a “simple” common observable, gives an extraordinary rich opportunity for future research in clathrate science and other fields. The limitation of neutron scattering for the investigation of clathrate hydrates (and for many other systems) is probably linked to the difficulty of preparing a large single crystal. Nevertheless, this limitation will probably be overcome in the near future with the opportunity of using small samples because of the construction of high-brilliance neutron source like the European Spallation Source at Lund (Sweden) and to the development of highly sensitive neutron instruments on existing high-brilliance reactor-based sources and on future small/medium-brilliance sources. Such technological evolution of the neutron sources and instruments will finally be a real breakthrough for \textit{in situ} or \textit{operando} experiments on clathrate hydrates.

1.6. Bibliography


