Harald Conrad (Editor)

**Advanced Cold Moderators**

**AcoM-6**
Proceedings of the 6th International Workshop on Advanced Cold Moderators
held at Forschungszentrum Jülich
from 11 to 13 September 2002

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Preface

These are the Proceedings of the 6th Meeting of the International Collaboration on Advanced Cold Moderators. We apologize for the long delay in publishing these lecture notes, which is mainly the editor’s fault. On the other hand, despite the long time since our meeting, it was not possible to obtain all contributions to the Proceedings in full text version. Like in the editor’s case this is certainly due to the many other duties of our colleagues. In order to nevertheless present a complete account of the meeting we have included in an Appendix copies of what was collected from the authors during the meeting.

The collaboration on Advanced Cold Moderators was initiated during a meeting at Forschungszentrum Jülich in July of 1997, when a small working group of experts from numerous institutions was established. After this inaugural meeting we had the second one, arranged by Renate Bercher and Günter Bauer of the Paul-Scherrer-Institut in Villigen (Switzerland) in February of 1998. The third meeting, ACoM-3, took place in Oak Ridge under the supervision of Trevor Lukas in June of the same year. The fourth meeting was organized by Heidrun Barnert-Wiemer of Forschungszentrum Jülich and held there in February of 1999. The fifth meeting took place in Berlin in connexion with a general workshop on moderator concepts for spallation sources organized by Thomas Gutberlet, then at the Hahn-Meitner-Institut in Berlin.

Of the first three meetings only minutes were written up and supplemented with copies of a few presentations, which were available. The first “formal” proceedings were printed and distributed among the collaboration members and meeting participants for ACoM-4.

Our sixth meeting, the proceedings of which we deliver here, was attended by thirty-four colleagues from eight countries on three continents – a small but impressive assembly of experts in the field. They presented their latest results in theory, numerical computation and experiments on advanced cold moderator media like methane-hydrate, tri-methyl-benzene or ammonia. With the sponsorship of Forschungszentrum Jülich and the support of members of the project team of the European Spallation Source (ESS) we were able to have a pleasant and fruitful meeting on site in the seminar room of the ESS project building. Taking care of transportation and hotel accommodation of the external participants, the ladies Julia Philippen and Andrea Fournier warranted a smooth course of the meeting. Lunches were served in one of Forschungszentrum’s Cafeterias and coffee and snacks during the breaks were provided next to the lecture hall. Günter Mank and Alf Bauer from the ESS project team efficiently assisted with technical support regarding computers and beamer facilities.

The European Spallation Source project is unfortunately dormant for an unspecified term and the two major megawatt spallation facilities in Japan and the US are in a very advanced stage of construction employing conventional cryogenic moderators only. Nevertheless, the performance prospects of advanced cold sources (if we consider an all para-hydrogen moderator a conventional one) are so intriguing that we can expect their development to continue. In this respect we are looking forward to our next meeting.

Harald Conrad, editor
March 2004
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ABSTRACT

For the calculation of neutron spectra in cold and super thermal sources scattering laws for a variety of liquid and solid cryogenic materials were evaluated and prepared for use in deterministic and Monte Carlo transport calculations. For moderator materials like liquid and solid H2O, liquid He, liquid D2O, liquid and solid H2 and D2, solid CH4 and structure materials such as Al, Bi, Pb, ZrHx, and graphite scattering law data and cross sections are available. The evaluated data were validated by comparison with measured cross sections and comparison of measured and calculated neutron spectra as far as available. Further applications are the calculation of production and transport and storing of ultra cold neutrons (UCN) in different UCN sources. The data structures of the evaluated data are prepared for the common S_N-transport codes and the Monte Carlo Code MCNP.

1. INTRODUCTION

For the optimisation of cold neutron sources transport and thermalisation calculations must be performed to get important parameters such as gain factors, heating rates and fluences for containers etc. For such transport and thermalisation calculations for all investigated moderators and structure materials realistic scattering laws must be available. There exist computer programs for the solution of the neutron transport equation based on the Monte Carlo method (MCNP-X [1]) or discrete ordinate S_N-method (DORT/TORT [2]). The scattering law data and transport and thermalisation calculations must be validated by corresponding experiments by comparing of measured and calculated cross sections and neutron spectra. At IKE since many years scattering law data were derived and evaluated for a number of moderators and different phase states. The present data, developed at IKE are the following:

- Liquid hydrogen as p-H2 and o-H2 at T = 14K and 20.38K
- Liquid deuterium as o-D2 and p-D2 at T = 19K and 23.65K
- Solid o-D2 at T = 5K, 10K, 13K and 17K
- Solid p-H2 at T = 5K, 6K and 13K
- Gaseous hydrogen as p-H2 and o-H2 at T = 20.38K and 25K
- Gaseous deuterium as o-D2 and p-D2 at T = 23.65K
- Liquid helium as 4He at T = 1K (UCN-production)
- Bismuth at T = 77K and 293.6K
- Beryllium at T = 2.5K and 25K
- Aluminium at T = 20K, 100K and 293.6K
- Lead at T = 293.6K
- Heavy Water as D(D2O), O(D2O) + all other interference terms at T = 293.6K
The data are available as $S(\alpha,\beta)$ scattering laws with detailed $\alpha,\beta$ grids and MCNP thermal scattering data or multigroup transport data in 150 thermal groups. For ultra cold neutrons special group structures and MCNP data were generated up to $10^{-10}$ eV.

2. INVESTIGATION OF THE NEUTRON SCATTERING DYNAMICS AND THERMALISATION IN SOLID AND LIQUID LIGHT WATER

2.1 General

Light water is a very important moderator material used over a wide temperature range in power reactors, research reactors or for cold neutron sources. To deliver realistic data sets for standard neutron cross section libraries as ENDF/B [3], JEF [4], JENDL [5] or for MCNP [1] the neutron scattering dynamics in the different phases of the moderator must be well understood to describe the energy and momentum transfer of thermal neutron scattering. For H bound in H$_2$O the singlet and triplet neutron scattering amplitudes or scattering lengths differ very much. So in every phase the commonly used incoherent approximation is a tolerable assumption. The error in the cross section data may be in the order of about 2%. For all phases discussed, the neutron-scatterer interaction is pronounced by the individual dynamical excitations of the scatterer. Generally these may be divided into translational modes at low frequencies, which essentially are intermolecular interactions and optical modes which may be handled as discrete oscillations at higher energies and which stand for intra-molecular interactions. Of course, if water is not in the condensed phase, the H$_2$O molecules may rotate free. For the single H$_2$O molecule with its non-linear structure, generally, there are 3N degrees of freedom. With N=3 atoms in the molecule these degrees of freedom divide into 3 for translational motion, 3 rotations and 3 oscillations. In the literature, these different motions generally are discussed to derive more or less quantitative models for the neutron scattering dynamics in a condensed or uncondensed phase of light water. In the following, we give a survey about the models derived at IKE for the individual phase and compare it with assumptions of other authors. The derived frequency distributions are then input for the codes LEAPR of the NJOY code package [6] or GASKET2 [7] (modified at IKE) to generate Scattering Law files in ENDF-6 format. For the chosen $\alpha,\beta$ grid of the $S(\alpha,\beta)$ care must be taken to ensure a closely correlation to the important domains of $\rho(\omega)$. For quality assurance of the prepared files, a lot of differential and integral neutron cross sections are compared with measurements. In addition, other parameters closely correlated to the phonon spectra as heat capacity, effective neutron scattering temperature or average scattering amplitude of the scattering nucleus are investigated. To test the neutron thermalisation, neutron flux spectra are calculated and compared with experimental ones.

2.2 Solid H$_2$O, ice

At normal conditions liquid water crystallises as hexagonal close packed (hcp) ice classified as modification Ih. To understand this structure, one can imagine that the H$_2$O molecule is located as a first approximation at a lattice point of the hcp lattice. Whereas the molecular translations are strongly hindered as do the hindered rotations to some extent, the intramolecular oscillations may be treated as relatively free motions. In the literature, there exist different assumptions for the three mode motions to derive a generalised frequency distribu-
tion, which is the base to generate cross section data sets. For the hindered translations, the most quantitative information is given by Nakahara [8], who used the root sampling method to obtain the dispersion relations and the phonon spectrum of ice. For our model, we have smoothed out his histogram values to get the lower energy part of Fig. 1. Other models for this part are known from Prask et. al. [9], Burgman et al. [10], or Renker [11], who derived the low energy spectrum from time-of-flight measurements of inelastic scattered neutrons in hcp ice. This method of course is somewhat problematic, because multiphonon excitations of the lowest peaks influence the higher energy part and a quantitative correction is difficult. Other authors as Tewari et. al. [12] assumed Debye spectra for this energy region with Debye temperatures around 250 K. For the solid state of water, the translational weight of the frequency distribution should be approximately 1/18, as is generally demonstrated by Kadotani et al. [13].

For the high frequency intramolecular oscillations the assumption of discrete harmonic Einstein $\delta$-oscillators is a good approximation, whereas for the asymmetric scattering modes the frequencies are nearly identical. So they are handled as degenerated with doubled weight. The detailed frequencies are listed for the three phases in Table 1. Compared to formerly publications we have modified the values, especially for liquid water and water vapour. Compared to our treatment of H in polyethylene [14], we have set the weight of the intramolecular oscillations to 0.5 in the complete frequency distribution, which is consistent to the assumption for the light water data of ENDF/B-6 published in the Kernel Book [15]. As we have shown in our studies for H in polyethylene, the individual weights of the 3 oscillations and the 3 hindered rotations are nearly identical. Therefore the weight of the oscillations should be a little bit smaller than 0.5. But being consistent with our models for the liquid and gaseous phase we neglect this.

In the condensed phases, the hindered rotations cover a broad band of frequencies. Compared to the liquid the solid binding is stronger, resulting in an increase of the band peak of about 12%. For our model of H in H$_2$O in Ih ice we have designed a Doppler broadened gaussian peak around 75.6 meV weighted to 0.5 – 1/18. The shape is shown in the upper energy range of Fig. 1. In contrast to other authors as Nakahara [8] or Tewari et. al. [12] we assume for the hindered rotational level an Einstein $\delta$-oscillator. The consequence is a very narrow peak, which is not realistic for the condensed phase from physical aspects.

Contrary to our model for the liquid phase the continuous frequency distribution for light water ice (see Fig. 1) is assumed to be temperature independent. This means that it is handled in harmonic approximation.

Table 1. Intramolecular oscillator frequencies of H in H$_2$O in eV

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</table>

Light water ice is of special interest as a cold moderator in the temperature range of some K up to about 10-20 K. To test the quality especially of the translational part of the frequency distribution we calculated the heat capacity and compared it with experimental data [16] and with a commonly used Debye model. As is clearly seen from Fig. 2 our model is superieur to a simple treatment.

To examine the quality of the generated phonon spectrum for water ice Ih comparisons were done for differential and integral neutron cross section measurements. To do this for a lot of temperatures Scattering Law files in ENDF-6 format must be calculated. This was done either with the LEAPR code of the NJOY code system or with the IKE version of GASKET2.
In Table 2 a survey is given about the temperature grid of the Scattering Law files. In addition, in this table values for the effective neutron scattering temperature \( T_{\text{eff}} \), the Debye-Waller integral DWI, and the average scattering amplitude \( \langle u \rangle \) of the bound H are listed. \( T_{\text{eff}} \) is used for calculating scattering law data outside of the stored \( \alpha, \beta \) grid according to the short collision time approximation and the DWI is used for the generation of the incoherent elastic neutron scattering data.

**Figure 1.** Continuous part of the frequency distribution of H bound in light water ice

**Figure 2.** Heat capacity of light water ice
Table 2. Generated Scattering Law files for H in H$_2$O and parameters correlated to the phonon spectrum

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>$T_{\text{eff}}$ / K</th>
<th>DWI / eV$^{-1}$</th>
<th>$&lt; u &gt;$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1188.7</td>
<td>12.08</td>
<td>0.158</td>
</tr>
<tr>
<td>20</td>
<td>1188.7</td>
<td>13.24</td>
<td>0.166</td>
</tr>
<tr>
<td>77</td>
<td>1189.7</td>
<td>20.34</td>
<td>0.205</td>
</tr>
<tr>
<td>113.2</td>
<td>1191.1</td>
<td>25.42</td>
<td>0.230</td>
</tr>
<tr>
<td>165.2</td>
<td>1195.4</td>
<td>33.00</td>
<td>0.262</td>
</tr>
<tr>
<td>186</td>
<td>1198.2</td>
<td>36.10</td>
<td>0.274</td>
</tr>
<tr>
<td>218.2</td>
<td>1203.5</td>
<td>40.95</td>
<td>0.291</td>
</tr>
<tr>
<td>248.8</td>
<td>1209.9</td>
<td>45.63</td>
<td>0.308</td>
</tr>
<tr>
<td>258.2</td>
<td>1212.1</td>
<td>47.07</td>
<td>0.312</td>
</tr>
<tr>
<td>273</td>
<td>1215.8</td>
<td>49.36</td>
<td>0.320</td>
</tr>
</tbody>
</table>

Figure 3. Differential neutron scattering cross section in water ice at 218.2K (E0=39 meV)

Among the numerous recalculated neutron cross section experiments we present here an angular distribution (Fig. 3, [17]), the total neutron cross section (Fig. 4, [18]) and the average cosine of the neutron scattering angle (Fig. 5, [17]) for different temperatures. A first test of the calculated cross section data and the processed MCNP data sets two thermalisation experiments with pure moderator systems [45] were recalculated. For two experiments (Inoue et al. [45]) with ice of 20 K and 77 K respectively the neutron spectra in the re-entrant hole were measured and calculated. The results are shown in Fig. 6 and Fig. 7, respectively. The calculated and measured spectra were normalised according to the 1/E range. The calculated flux density spectra agree well with the corresponding measured spectra, especially for 20 K. The geometrical model was only roughly described in the publication of Inoue et al. Therefore, the shown results may be biased due to this uncertainty.
Figure 4. Total neutron cross section of water around T = 273K

Figure 5. Average cosine of the neutron scattering angle in water ice at T = -15°C
Figure 6. Neutron flux density spectrum in light water ice at T=20K

Figure 7. Neutron flux density spectrum in light water ice at T=77K
2.3 Liquid water

Compared to the solid state liquid water shows some modifications in the binding relations of the H₂O molecules. Springer [18] has discussed in detail these effects. Following the model assumptions of Eucken [19] and considering the experimental data of Haywood, Page [20] we have generated a model for the complete dynamical modes treatment constructing a generalised frequency distribution for H bound in liquid water. Details are published by Keinert, Mattes [21]. The Scattering Law Data generated at IKE with this model were integrated into the JEF data libraries [3]. Details are given in the JEF documentation [22]. Compared to the model based on the ENDF/B-6 data files our model treats the hindered translations as well as the hindered rotations being temperature dependent, whereas in ENDF/B these modes are treated in harmonic approximation. In our model for H bound in H₂O in the liquid phase the scattering dynamics modes are treated according to following assumptions:

- hindered translations with effective temperature dependent masses. The temperatures of the generated $S(\alpha,\beta)$ data are listed in Table 3. The moving translational units can be thought to be clusters of single molecules as well as two fold, four fold, and eight fold complexes of H₂O molecules with varying frequencies depending on temperature.
- hindered rotations with a broad band of frequencies are temperature dependent as it is shown in Fig. 8. In this figure also a comparison is made with the temperature independent curve taken for ENDF/B-6 [15]. Considering a special temperature, the wanted frequency distribution is interpolated from the limiting curves.
- two Einstein $\delta$-oscillators are used for the description of corresponding symmetric and asymmetric vibrations of the water molecule. Compared to our model for the JEF data [19] the frequencies of the degenerated asymmetric vibrations are slightly reduced taking into account the liquid state.

<table>
<thead>
<tr>
<th>T / K</th>
<th>T_eff / K</th>
<th>DW1 / eV⁻¹</th>
<th>&lt;υ&gt; / Å</th>
<th>M_trans /amu</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.2</td>
<td>1309.8</td>
<td>11.15</td>
<td>0.152</td>
<td>53.30</td>
</tr>
<tr>
<td>278.2</td>
<td>1310.7</td>
<td>11.22</td>
<td>0.153</td>
<td>51.32</td>
</tr>
<tr>
<td>293.6</td>
<td>1313.7</td>
<td>11.45</td>
<td>0.154</td>
<td>46.00</td>
</tr>
<tr>
<td>308.6</td>
<td>1316.8</td>
<td>11.67</td>
<td>0.156</td>
<td>42.29</td>
</tr>
<tr>
<td>323.6</td>
<td>1320.1</td>
<td>11.89</td>
<td>0.157</td>
<td>39.00</td>
</tr>
<tr>
<td>348.6</td>
<td>1326.2</td>
<td>12.27</td>
<td>0.160</td>
<td>34.50</td>
</tr>
<tr>
<td>373.6</td>
<td>1332.9</td>
<td>12.65</td>
<td>0.162</td>
<td>31.00</td>
</tr>
<tr>
<td>398.6</td>
<td>1340.3</td>
<td>13.04</td>
<td>0.164</td>
<td>28.75</td>
</tr>
<tr>
<td>423.6</td>
<td>1348.2</td>
<td>13.45</td>
<td>0.167</td>
<td>27.00</td>
</tr>
<tr>
<td>448.6</td>
<td>1356.8</td>
<td>13.89</td>
<td>0.170</td>
<td>26.00</td>
</tr>
<tr>
<td>473.6</td>
<td>1365.8</td>
<td>14.32</td>
<td>0.172</td>
<td>25.00</td>
</tr>
<tr>
<td>498.6</td>
<td>1375.2</td>
<td>14.74</td>
<td>0.175</td>
<td>23.87</td>
</tr>
<tr>
<td>523.6</td>
<td>1385.0</td>
<td>15.17</td>
<td>0.177</td>
<td>23.00</td>
</tr>
<tr>
<td>548.6</td>
<td>1395.3</td>
<td>15.62</td>
<td>0.180</td>
<td>22.50</td>
</tr>
<tr>
<td>573.6</td>
<td>1406.0</td>
<td>16.07</td>
<td>0.183</td>
<td>22.00</td>
</tr>
<tr>
<td>598.6</td>
<td>1417.0</td>
<td>16.51</td>
<td>0.185</td>
<td>21.55</td>
</tr>
<tr>
<td>623.6</td>
<td>1428.3</td>
<td>16.95</td>
<td>0.188</td>
<td>21.00</td>
</tr>
<tr>
<td>647.2</td>
<td>1439.3</td>
<td>17.40</td>
<td>0.190</td>
<td>20.40</td>
</tr>
</tbody>
</table>
The generalised frequency distributions were taken to generate Scattering Law files in ENDF-6 format for several temperatures. The chosen temperature grid is given in Table 3. Additionally, there are also shown the effective scattering temperature, the Debye-Waller integral and the average scattering amplitude of the bound hydrogen. These parameters simply are correlated to the chosen frequency distribution $\rho(\omega)$. The upper temperature is near the critical temperature of 647.4 K.

From the stored Scattering Law files many differential and integral neutron cross sections are calculated and compared with experiments. In the following figures some plots are
presented. The corresponding experimental data were taken from [23-27]. For neutron thermalisation studies in liquid light water MCNP data sets are generated with the NJOY code system [6] and neutron flux spectra calculated with MCNP are compared with measured ones of different experimental arrangements.

Figure 10. Total neutron cross section of water at room temperature

Figure 11. Average cosine of the neutron scattering angle in water at room temperature
2.4 Conclusions for H$_2$O

For light water in its phases solid and liquid we have derived realistic models to describe the neutron scattering dynamics as a function of energy transfer, impulse change and moderator temperature. In addition, we discussed other model assumptions published and showed consequences to calculated neutron scattering cross sections. For our models the overall agreement with measured cross section data proved satisfactory. The cross section sets were generated for a distinct temperature grid and stored in ENDF-6 format. For thermalisation studies data sets for neutron transport codes as MCNP are generated as energy point libraries or as multigroup libraries for deterministic codes in 309 neutron energy groups.

3. HYDROGEN AND DEUTERIUM

3.1 General

The molecular dynamics of hydrogen and deuterium is determined by the motion of the either free H$_2$ or D$_2$ molecules (gaseous phase) or the bound state (condensed phase). Caused by the different two possible spin correlation there exist two molecular modifications (ortho and para). The ground-states are p-H$_2$ and o-D$_2$ (low spin value); the excited states are o-H$_2$ and p-D$_2$. The general formalism of neutron scattering in the condensed phases is presented in chapter 3.4. Important physical properties for the two cold moderators are given in table 4.

Table 4. Physical properties of deuterium and hydrogen at standard conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>D$_2$</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperature [K]</td>
<td>18.72</td>
<td>13.95</td>
</tr>
<tr>
<td>Boiling temperature [K]</td>
<td>23.65</td>
<td>20.38</td>
</tr>
<tr>
<td>Hcp lattice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a [Å]</td>
<td>3.605</td>
<td>3.782</td>
</tr>
<tr>
<td>c [Å]</td>
<td>5.882</td>
<td>6.167</td>
</tr>
<tr>
<td>Density [g/cm$^3$]</td>
<td>0.204</td>
<td>0.089</td>
</tr>
<tr>
<td>Atomic distance [Å]</td>
<td>0.748</td>
<td>0.751</td>
</tr>
<tr>
<td>Rotator energy [meV]</td>
<td>7.42</td>
<td>14.71</td>
</tr>
<tr>
<td>Oscillator energy [meV]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid</td>
<td>371</td>
<td>516</td>
</tr>
<tr>
<td>Gas, liquid</td>
<td>386</td>
<td>546</td>
</tr>
<tr>
<td>Bound atom scattering cross section [barn]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coherent</td>
<td>5.604</td>
<td>1.705</td>
</tr>
<tr>
<td>Incoherent</td>
<td>2.043</td>
<td>80.275</td>
</tr>
<tr>
<td>Scattering length b, [fm]</td>
<td>6.678</td>
<td>-3.683</td>
</tr>
<tr>
<td>Absorption cross section [mbarn]</td>
<td>0.056</td>
<td>332</td>
</tr>
</tbody>
</table>
3.2 Gaseous hydrogen and deuterium

The H$_2$ or D$_2$ molecules have 6 degrees of freedom, which can be subdivided into translations (3), free rotations (2) and oscillation (1). The acoustic modes therefore are weighted to 0.5. From the optical modes, the oscillation is weighted to 1/6. For the gaseous moderator the acoustic part of the frequency distribution is degenerated to a Delta-function at $\omega = 0$. The neutron scattering dynamics is described by the interaction of the neutron with a free molecule. Since the scattered waves from different molecules have no phase relations, only intra-molecular scattering takes place. Interference scattering is not possible. Koppel, Young [28] have derived the scattering theory for this case quantitatively. To get neutron cross-section data one must solve the Schrödinger equation for the system neutron and scattering molecules by use of the Fermi pseudo potential in the first Born approximation considering the molecular motions free translations, free rotations and harmonic oscillations to get the complete scattering function, which is the Fourier transformation of the Scattering Law $S(\alpha,\beta)$.

Since no computer program was available for us for the generation of cross-section data according to the general Koppel-Young theory, we implemented optionally the Koppel-Young formalism in our program SCATHD [29] for the different modifications and phases of hydrogen and deuterium.

3.3 Liquid hydrogen and deuterium

In the liquid phase the single molecules are condensed according to central force and quadrupole interaction. The translational modes therefore are smeared to a broad band in the frequency distribution. In Fig. 12 and 14 our results of an evaluation is shown. Compared to earlier publications (Keinert, [29, 41]), the models for the liquids are modified to a one peak curve considering new publications [43, 44] which are consistent with the relations in liquid water. The optical motions are nearly unchanged as free rotations and harmonic oscillations of the single molecule. In the liquid state the neutron interaction with the moderator molecules is complicated. The coherent scattered waves from a single molecule (intra) and the coherent scattered waves from different molecules (inter) can interfere. First of all, the intermediate scattering function of the translational part was generalised and integrated in the Koppel, Young formula by Emendörfer [29] The interference scattering was considered by deriving static structure factors $S(\kappa)$ (Fig. 13) (Keinert [29]) and integrating them by modification of the coherent scattering part according to the Vineyard approximation (see formalism in chapter 3.4). The Program SCATHD allows the calculation of Scattering Law Data $S(\alpha,\beta)$ according to this theory. Comparisons of differential and integral measured cross-sections with our calculated values show excellent agreement. Compared to earlier results [29] the effect of the altered frequency distribution is very small. SCATHD calculates all neutron scattering components (coherent as well as incoherent) in the S(\alpha,\beta) section of the ENDF/B-File (MF=7, MT=4) for the liquid phase and integrates it.
Figure 12. Frequency Distributions of the Acoustical Modes in Deuterium

Figure 13. IKE Static structure factors of liquid Hydrogen and Deuterium
Figure 14. Frequency Distributions of the Acoustical Modes in Hydrogen

3.4 Formalism of neutron scattering in condensed deuterium and hydrogen [29]

- Generalised double-differential scattering cross-section for the condensed phase (for example as a liquid)
  \[
  \frac{d^2 \sigma}{d\Omega d\varepsilon} = \frac{k}{k_0} \left[ b_\text{coh}^2 S^{bg \text{ coh} \text{ coh}}(\kappa, \varepsilon) + b_\text{inc}^2 S^{bg \text{ inc} \text{ inc}}(\kappa, \varepsilon) \right] + b_\text{coh}^2 S^{bg \text{ coh} \text{ inc}}(\kappa, \varepsilon)
  \]

\( S(\kappa, \varepsilon) \) - scattering Law for coherent and incoherent neutron scattering

\( b_\text{coh,inc} \) - scattering length for coherent and incoherent neutron scattering

\( \kappa = k_0 - k \) - neutron momentum transfer

\( \varepsilon = E - E_0 \) - neutron energy transfer

- approximation according to Vineyard
  \[
  \frac{d^2 \sigma}{d\Omega d\varepsilon} = \frac{k}{k_0} \left[ b_\text{coh}^2 S^{bg \text{ coh} \text{ coh}}(\kappa, \varepsilon) S(\kappa) + b_\text{inc}^2 S^{bg \text{ inc} \text{ inc}}(\kappa, \varepsilon) \right]
  \]

\( S(\kappa) \) - static structure factor of the liquid

- partial scattering laws
  \[
  S^{bg \text{ coh}}(\kappa, \varepsilon) = \sum_{J=even} P_J \sum_{J=odd} (2J + 1) \frac{1}{n!} \left( \frac{\hbar^2}{4M\omega} \right)^{\frac{1}{2}} \sum_{|J|} \sum_{J} C^2(J J; 0 0) S^{bg \text{ coh}}(\kappa, \varepsilon_{\text{eff}})
  \]

  conservation of energy principle \( \varepsilon_{\text{eff}} = \varepsilon + nh\omega + E_j - E_j \)

\( C^2(J J; 0 0) \) - Clebsch-Gordan coefficients
• Matrix-Elements

\[ A_{\mu} = \int_{\mu=1}^{2} P_{\mu}(\mu) \mu^{\mu} \exp\left(-\frac{\mu^{2} K^{2} h}{8M\omega} + i \left( R_{\mu} \mu^{\mu} \right) \right) d\mu \]

• Generalised formulas for the different modifications of the cold moderators (for example in the liquid state)

**Para-Hydrogen (S = 0):**

\[
\frac{d^{2} \sigma}{d\Omega d\epsilon} = \frac{k}{k_0} \left[ b_{\text{coh}}^{2} \epsilon S(\kappa) S_{\text{coh}}(\kappa, \epsilon) + b_{\text{inc}}^{2} \epsilon S_{\text{inc}}(\kappa, \epsilon) \right]
\]

**Ortho-Hydrogen (S = 1):**

\[
\frac{d^{2} \sigma}{d\Omega d\epsilon} = \frac{k}{k_0} \left[ \frac{1}{3} b_{\text{coh}}^{2} \epsilon S_{\text{coh}}(\kappa, \epsilon) + \left( b_{\text{coh}}^{2} \epsilon S_{\text{coh}}(\kappa, \epsilon) + \frac{2}{3} b_{\text{inc}}^{2} \epsilon S_{\text{inc}}(\kappa, \epsilon) \right) \right]
\]

**Ortho-Deuterium (S = 0.2):**

\[
\frac{d^{2} \sigma}{d\Omega d\epsilon} = \frac{k}{k_0} \left[ b_{\text{coh}}^{2} \epsilon S_{\text{coh}}(\kappa, \epsilon) + \frac{5}{8} b_{\text{inc}}^{2} \epsilon S_{\text{inc}}(\kappa, \epsilon) + \frac{3}{8} b_{\text{inc}}^{2} \epsilon S_{\text{inc}}(\kappa, \epsilon) \right]
\]

**Para-Deuterium (S = 1):**

\[
\frac{d^{2} \sigma}{d\Omega d\epsilon} = \frac{k}{k_0} \left[ \frac{3}{4} b_{\text{coh}}^{2} \epsilon S_{\text{coh}}(\kappa, \epsilon) + \left( b_{\text{coh}}^{2} \epsilon S_{\text{coh}}(\kappa, \epsilon) + \frac{1}{4} b_{\text{inc}}^{2} \epsilon S_{\text{inc}}(\kappa, \epsilon) \right) \right]
\]

The Program SCATHD calculates \([\ldots] / b^{2}\) as Scattering Law file in ENDF/B-6 format for MT=7 and MF=4.

For the liquid phase S(α, β) contains the complete scattering information, including Intra- as well as Inter-interference. In generating integral cross-section data, for \(\sigma_{\gamma}\) to the scattering cross-section only the neutron absorption cross-section must be added.

In the solid phase S(α, β) contains quantitatively the inelastic Intra-scattering. The coherent and incoherent elastic scattering must be added.

For the gaseous phase a Scattering Law according to the quantitative Koppel, Young-Ansatz may be calculated with SCATHD containing all scattering components.

### 3.5 Solid hydrogen and deuterium

Solid hydrogen and deuterium have a polycrystalline lattice structure in a wide temperature range (2-4 K) according to hexagonal close packed (hcp) lattices like metallic Be or BeO. At lower temperatures the lattice structure can change to face centered cubic (fcc), which for hydrogen for example is dependent on the content of o-H2.

The translatoric motion in the lattice is well known [31, 35, 36]. The frequency distribution of the acoustical modes is pronounced by lattice-forces like van der Waals, overlapping and quadrupole-quadrupole. As shown in the Figs. 12 and 14 the data of Yu et al. are taken in harmonic approximation. For the optical modes, in the solid phase there are some uncertainties. Some authors assume [31, 34], that due to the low temperature in the moderator (degrees of freedom are frozen) and the low energy neutron source spectra these modes must not be considered. Others suppose [37], that the molecule at the lattice position can rotate...
relatively free and can also suffer excitation of the oscillation if the neutron energy is large enough (neutron downscattering). To examine this, in the following we calculate cross-section data for these two models for the moderator used as a source of UCN (o-D$_2$ at 5K). But first we must take care of the fact that the neutron scattering dynamics is completely different from that of the liquid phase, so that SCATHD is not generally adequate.

For the hcp-lattice the coherent elastic scattering cross-section may be calculated by a code like HEXSCAT [38] Therefore by using SCATHD the inter interference scattering must be switched out (set $S(\kappa) = 1$). Then in SCATHD only intra scattering without intermolecular interference is calculated. Generating Scattering Law Data with SCATHD or GASKET2 [7], in addition one must take care of that the elastic part ($\beta=0$) of $S(\alpha,\beta)$ is handled in incoherent approximation. Therefore the incoherent elastic part should be calculated separately (set parameter NDAM=1 in GASKET2 and for the resulting $S(\alpha,\beta)$ generated with SCATHD set 0.0 for $\beta=0$). The formula for the incoherent elastic cross-section is quite simple:

$$\sigma_{inc-el}(E) = \sigma_{b-inc} \cdot A \cdot \left( 1 - \exp \left( -4 \cdot E \cdot \gamma(0) / A \right) \right) / \left( 4 \cdot E \cdot \gamma(0) \right)$$

$\gamma(0)$ is the Debye-Waller integral for the frequency distribution part to be considered.

Generally, generating ENDF/B-Files, there exists a problem for the compilation of coherent as well as incoherent elastic scattering data. Normally, in ENDF/B there are either coherent or incoherent elastic scattering cross-sections in section MF=7, MT=2. Both data sets are not foreseen, but for solid deuterium, for example, the incoherent elastic scattering is about 26% of the complete part, an amount which must be considered.

3.5.1 Cross-section data for o-D$_2$ (theory model 1)

For the dynamic modes and the scattering components of model 1 we make the following assumptions:

- the degrees of freedom for rotation and oscillation are frozen
- frequency distribution for the acoustical modes as in Fig. 12, normalised to 1.0
- only inelastic scattering in $S(\alpha,\beta)$, incoherent approximation, parameter NDAM=1 in GASKET2
- coherent elastic scattering calculated separately by HEXSCAT/IKE
- incoherent elastic scattering calculated separately (program ELAS)

The partial total scattering cross-sections for o-D$_2$ at 17K are plotted in Fig. 15. As from the coherent scattering cross-section can be seen, the Bragg edge for solid deuterium is at 2.098 meV. For smaller neutron energies the scattering is completely incoherent. This fact is important in discussing the interaction of UCN with matter in solid deuterium.
3.5.2 Cross-section data for o-D₂ and p-H₂ (theory model 2)

Compared to the assumptions for the scattering dynamics model 1 for the solid moderator, following it is implemented:

- the degrees of freedom for rotation and oscillation can be excited, program SCATHD for \( S(\alpha, \beta) \) (with \( S(\kappa) = 1 \), NDAM=1 and \( S(\alpha, \beta = 0) = 0.0 \)) inelastic Intra-scattering handled exactly, no incoherent approximation
- frequency distribution for the acoustical modes normalised to 0.5
- coherent elastic scattering by HEXSCAT/IKE, modified Debye-Waller integral for o-D₂
- no incoherent elastic scattering from the acoustic modes for p-H₂ up to \( \omega_{\text{rot}} \), modified Debye-Waller integral for o-D₂ and p-H₂

In Fig. 15 the partial scattering cross-sections for model 2 are compared to those generated with model 1 for solid deuterium. As it is clearly seen, the main difference is from the modification of the Debye-Waller integrals caused by the altered frequency distributions used for coherent and incoherent elastic neutron scattering. Looking for the inelastic neutron scattering, the excitation of the rotator for model 2 is obvious.

3.5.3 Verification of the models, comparison with experimental data

For the solid moderators only few experimental data correlated with the frequency spectra \( \rho(\omega) \) or the neutron scattering dynamics are known. Hill, Lounasmaa [36] measured the specific heat \( C_v \) for solid deuterium. \( C_v/3R \) is simply correlated to \( \rho(\omega) \), especially for the acoustical branch, according to:

\[
C_v / 3R = \int \rho(\omega) \cdot (\omega / T)^2 \cdot \exp(\omega / T) / (\exp(\omega / T) - 1)^2 \ d\omega
\]

In Fig. 16 a comparison is shown for the theoretical models and the experiment. It seems, that model 2 gives the best agreement to the experimental values.
Seiffert [40] has measured total neutron cross-sections for solid hydrogen and deuterium. To compare with the experiment, we must combine the partial cross sections for scattering (inelastic and elastic incoherent and coherent) with absorption for our two models. In Fig. 17 the result is shown for deuterium (probably n-D$_2$). As it is clearly seen from the rotational peak around 10 meV, the rotations (and the oscillation) are not frozen. Therefore, the model 1 is not realistic for the solid moderators. The strong decrease of the measured cross-sections around 2.3 meV may be caused by great single crystallic domains in the probe, whereas we calculated the coherent part for pure polycrystallic moderators.

In Fig. 18 our results are presented for $\sigma_T$ (E) of p-H$_2$; but only for the model 2 calculations are done. As it is obvious, from the strong increase of the cross-section at $E > \omega_{\text{rot}}$ (excitation of the rotator), the neglecting of the optical modes in model 1 cannot lead to realistic cross-sections.
Over a wide energy range our data are in excellent agreement with the experiment. Therefore it is stated from the comparison for p-H₂ (better than from deuterium), that the optical modes may be excited in the solid moderators under the conditions of working with cold neutron sources for the production of ultracold neutrons.

Figure 18. Total Neutron Cross-Sections for Solid hcp p-Hydrogen at 5K

3.6 SOLID DEUTERIUM AS A COLD NEUTRON SOURCE PRODUCING ULTRACOLD NEUTRONS (UCN)

For design studies of existing [34] or planned [42] sources of ultracold neutrons extensive radiation transport calculations must be done. But determining the ucn density, nowadays no standard transport code is generally available to calculate realistic neutron spectrum data in the ultracold neutron energy range. Most of the known codes are restricted to energies greater than some $10^{-5}$ eV from numerical aspects. Therefore, one must calculate the neutron flux spectrum for the cold neutron domain and then determine the production rate of ucn by the downscattering rate of the thermal and cold neutrons coming from the cold neutron source of the research reactor. Unfortunately, this method too delivers no spectral information for the loss rate of ucn, which essentially is the upscattering rate and the absorption rate. For our discussion, we therefore assume from our experience of studies with cold neutron sources in the liquid phase [29] that the neutron flux spectrum in a solid deuterium neutron source can be approximated as first guess by a maxwellian shape with a neutron temperature around 30K plus an $1/E$ slowing down flux with a cut-off around 40 meV.

3.7 UCN PRODUCTION RATE FROM DOWNSCATTERING OF COLD NEUTRONS

The downscattering rate of cold and thermal neutrons to the ucn energy range from $10^{-9}$ to $10^{-6}$ eV generally describes the ucn production:

$$PR(E_{ucn}) \, dE_{ucn} = N \int \sigma_s (E_i \rightarrow E_{ucn}) \cdot \Phi (E_i) \, dE_i \, dE_{ucn} \, [\text{ucn} / \text{cm}^3 / \text{s}]$$

The energy range for integration is dominated by the structure of the differential downscattering cross-section of the solid material. Cause in solid deuterium there may be some amount of hydrogen (normally around 0.2 wt%) in Fig. 19 this cross-section is plotted for
o-D$_2$ and p-H$_2$ at 5K for an ucn energy of 200 neV. As is seen, the lower integration limit for PR (E-ucn) may be 10$^{-5}$ eV. For pure deuterium, the upper energy limit may be around 20 meV. But for deuterium and hydrogen mixtures this limit must be increased to 300 meV. The differential downscattering rate will be dominated by the structure around some meV up to 30 meV which clearly is correlated to the acoustical and rotational modes of the frequency distributions (resonance scattering). Therefore one must take care of the production of adequate Scattering Law Data. In S(α,β) the α,β-grid generally must contain the dominant energy structures of these scatterer dynamic modes.

![Figure 19. Differential Scattering Cross Section for Solid hcp Moderators at 5K (E-UCN=200 neV)](image)

In Fig. 20 the calculated ucn production rates are presented for pure o-D$_2$ at different temperatures and the two models for the scatterer dynamics described in chapter 2. As is clearly seen, the temperature effect is not very significant and the more realistic model from physical aspects delivers slightly fewer ucn. Calculating a mixture of o-D$_2$ with 0.2 wt% p-H$_2$, the production rate of ucn remain nearly unchanged.

### 3.8 UCN LOSS RATE FROM NEUTRON UPSCATTERING AND ABSORPTION

Contrary to realistic cold neutron source calculations, where no spectral informations of the ucn energy range exist, we are able by our approximation with a maxwellian flux density to estimate the ucn upscattering and absorption rates. The ucn loss rate is calculated as:

$$LR (E–ucn) dE-ucn = N \Phi (E-ucn) \left[ \sigma_A (E-ucn) + \int \sigma_s (E-ucn \rightarrow E_f) \, dE_f \right] dE-ucn$$

The final energy integration range begins at the end of the ucn energy domain. The complete integration range can be seen from Fig. 21 where the differential ucn upscattering cross-sections for o-D$_2$ and p-H$_2$ are drawn. Cause of the low temperature, compared to the downscattering cross-section, only poor fine structures of the frequency distribution modes can be seen here.
The UCN upscattering rates for the different dynamic scattering models and temperatures are presented in Fig. 22. As is clearly seen, it is not favourable to have a working temperature of an ucn source in the upper temperature range of the solid phase.
In Fig. 23 the absorption and upscattering rates of ucn are compared for the pure o-D$_2$ moderator and for a mixture with 0.2 wt% p-H$_2$. For the deuterium sample, the upscattering rate is slightly lower than the absorption rate. Taking the mixture, the upscattering rate remain nearly unchanged whereas the absorption rate is increased by a factor of 4 due to the large absorption cross-section of hydrogen.
4. SOLID METHANE AS A COLD MODERATOR

As a moderator for cold neutron sources methane essentially is discussed to be used in the solid phase with temperatures around 20 to 30K. In this temperature range methane crystallises in a face-centered cubic (fcc) lattice. The methane molecule CH₄ is built up as a tetrahedral structure of the hydrogen atoms with the carbon atom at the centre of mass. As for the solid hydrogen containing moderators like polyethylene or light water ice the neutron interaction with the bound H nuclei is treated in incoherent approximation. This can be done without significant loss of accuracy due to the strong dominance of the incoherent neutron scattering. Therefore, for simplification the coherent neutron scattering in the regular lattice can be omitted. The consequence of this approximation is that the neutron scattering below the Bragg edge will be slightly overestimated.

The methane molecule has N=5 atoms. Taking 3N degrees of freedom in the solid phase they split into 3 (hindered) translational modes, 3 strongly hindered rotations and 9 relatively free oscillations. Omitting the translational modes weight and assuming the optical modes being equivalently weighted, the part of the hindered rotational band in the frequency distribution for the bound hydrogen should be weighted approximately by 1/4, the part of the discrete oscillators should be weighted by 3/4. Following the ideas of MacFarlane [46] the 9 oscillators are reduced to 4 with corresponding parameters listed in Table 5.

Table 5. Optical modes data for H bound in solid methane

<table>
<thead>
<tr>
<th>mode</th>
<th>ω₁ (Vib./meV)</th>
<th>ω₂ (Rot./meV)</th>
<th>ω₃ (Meff/amu)</th>
<th>ω₄ (Rot./meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vib./meV</td>
<td>162</td>
<td>190</td>
<td>361</td>
<td>374</td>
</tr>
<tr>
<td>Mᵥᵤ/amu</td>
<td>3.247</td>
<td>5.376</td>
<td>23.81</td>
<td>6.944</td>
</tr>
<tr>
<td>Rot./meV</td>
<td>Smeared</td>
<td>Band</td>
<td>Maximum</td>
<td>8.0</td>
</tr>
<tr>
<td>Mᵥᵤ/amu</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.125</td>
</tr>
</tbody>
</table>

The smeared band of the hindered rotations in the frequency distribution is shown in Fig. 24 together with a proposal of Morishima et al [47]. The distribution given by MacFarlane is derived from the measurements of Harker, Brugger [48]. It is handled in harmonic approximation. Compared to the older ρ(ω) the new one has a lower weight which seems to be not adequate compared with measured total neutron cross sections of solid methane (Fig. 25). For the Morishima model the authors reduced the number of discrete oscillators to two (170 and 387 meV). Generating a Scattering Law data file with this model we have taken the same relative weight ratio as for the four oscillators. In Table 6 an overview is given for the temperature grid and the MCNP data sets. To validate the neutron transport model and the scattering dynamics some thermalisation moderator experiments [45, 49] with solid methane as moderator were recalculated. Compared to the measured neutron flux densities the calculated results agree well within the published accuracy (Fig. 26 and Fig. 27).

Table 6. Temperature grid of the generated data sets for H bound in solid methane

<table>
<thead>
<tr>
<th>T in K</th>
<th>20</th>
<th>22</th>
<th>31</th>
<th>57</th>
<th>77</th>
<th>89</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCNP set</td>
<td>s-meth.00t</td>
<td>s-meth.01t</td>
<td>s-meth.02t</td>
<td>s-meth.03t</td>
<td>s-meth.04t</td>
<td>s-meth.05t</td>
</tr>
</tbody>
</table>
Figure 24. Continuous part of the frequency distribution of H bound in solid methane around T=22K

Figure 25. Total neutron cross section for solid methane around T=20K
Figure 26. Neutron flux density spectrum in solid methane around T=20K

Figure 27. Neutron flux density spectrum in solid methane at T=20K

5. CROSS SECTIONS DATA SETS FOR POLYCRYSTALLINE ALUMINIUM

Aluminium metal crystallises at normal conditions in a face centered cubic (fcc) lattice structure. For cold moderators often it is used as a container material at low temperatures around 20K. To get optimally thermalised cold neutron flux spectra re-entrant holes often are implemented for these cold neutron sources with a wall thickness of 1-3 mm.

The neutron-scattering nucleus interaction in fcc Al is pronounced essentially by the dynamical modes excitation of the Al lattice describing neutron downscattering or upscattering. Käfer [50] examined these correlations evaluating a generalised frequency distribution
derived from Walker [52]. The neutron scattering in the Al lattice is composed by an incoherent inelastic scattering part generated as Scattering Law Data $S(\alpha,\beta,T)$ file in ENDF-6 format and the coherent elastic part.

In Fig. 28 the generalised frequency distribution $\rho(\omega)$ for polycrystalline Al is shown which is taken in harmonic approximation for calculating $S(\alpha,\beta,T)$. The contributions of the elastic and inelastic neutron scattering to the integral cross section is shown in Fig. 29. Comparisons of calculated and measured Al cross sections at 100K [50] showed good agreement, measurements at 20 K are not available (see also [51]).

![Figure 28. Frequency distribution of polycrystalline aluminium](image)

![Figure 29. Total cross sections for polycrystalline aluminium](image)
6. TRANSPORT CALCULATIONS FOR COLD AND ULTRA COLD NEUTRONS

The transport calculations based on the evaluated scattering laws can be performed with standard transport codes in multigroup approximation or by continuous Monte Carlo e.g. by the multigroup programs ANISN, DORT, TORT (Sₙ theory) or MORSE (Monte Carlo) and by continuous Monte Carlo codes like MCNP. The data processing for these codes can be performed by NJOY, if the scattering law data are available in corresponding ENDF-6 format. However, difficulties arise if the energy range of interest is lower than \(10^{-5}\) eV. For the range of ultracold neutrons (some neV to about 500 neV) the present NJOY version cannot process data. Therefore, we tried to extend all corresponding limits in NJOY to produce cross section data for multigroup and continuous Monte Carlo applications for the UCN range. This attempt was quite successful, we could produce data for solid, liquid and gaseous D₂ for various temperatures. For multigroup calculations no further changes in transport programs are necessary. The generated 277 group data with 79 groups below 0.01 meV, 33 groups up to 3 eV and 165 groups above 3 eV can be applied directly in standard Sₙ codes like ANISN. Continuous Monte Carlo calculations e.g. by MCNP, however, must be split into two parts. First part treats the energy range above the standard cutoff of 0.01 meV. The spectrum calculated by this part is then used to calculate the scattering source for the UCN range. A direct approach in one calculation leads to completely insufficient statistical results for extreme low energies. The separate calculation of scattering source will be performed based on the \(S(\alpha,\beta)\) scattering law data. This scattering source will be used then for a second run only for the UCN range. Using a biased source distribution the calculation for the UCN range results in spectra with sufficient statistical accuracy without extraordinary large computing time. As an example a simple model of a sphere was calculated to estimate the UCN production in a sphere filled by liquid and solid Deuterium of 20K and 10K, respectively. The sphere of 20 cm diameter was surrounded by a moderator of 293K. The outer diameter of the moderator was 150 cm. The problems were calculated by Sₙ code ANISN and MCNP (two parts, the space dependency of the scattering source in the inner sphere was regarded by subdividing the sphere into 10 regions). The results are shown in Fig. 30. The ANISN and MCNP results are in good agreement. The only problem found for the first part of calculation was in the range from 0.01 to 0.1 meV. Here, probably the procedure for treating the thermal scattering based on \(S(\alpha,\beta)\) tables should be improved. However, in the case of D₂ (liquid or solid) this range contributes not significantly to the UCN source.

![Figure 30. Comparison of ANISN and MCNP calculations for solid and liquid D₂ in a spherical container](image-url)
Since there is only a small gain of UCN per scattering UCN will be produced near neutron guides or in a storage with special treated surfaces to minimise their losses. In such regions total reflection must be regarded. This effect cannot be treated by the standard version of MCNP. Therefore, the reflection model for MCNP was extended to simulate reflection on mirrors or super mirrors by corresponding reflection law taking into account the losses at the walls of the guide tubes. The advantage of this application is that the geometry of the source and its environment can be treated for both spectrum calculation and UCN transport calculation by the same code. No special code for the UCN transport is necessary. All advantages of MCNP tally options for analysis of results can be used therefore. The only disadvantage is that gravity can only be regarded by further more complicated changes in reflection routine since the flight of neutrons in MCNP is simulated linearly. For calculation of neutron transport in a storage the decay of neutrons can be regarded by a special tally or by changing the weight after every boundary crossing event.

An application of MCNP for UCN production and transport in a UCN source is – for example – the calculation for the planned D₂ source in the FRM-II reactor which is presently in the start-up phase.

The cold source of liquid D₂ (Fig. 31) and the UCN source of solid D₂ (Fig. 32) is modelled in detail. In a first MCNP run the spectrum in the D₂ source (influenced from the cold source) is calculated. In second run MCNP transport calculations were started for the region of the solid D₂ and the storage for the UCN. The flow chart of these calculations is shown in Fig. 33. The results of such calculations are the production rate of UCN and the average life time of UCN in the storage taking into account losses at the wall and in the D₂ zone as well as the decay of neutrons.

![Image](https://example.com/image.png)

**Figure 31.** Detail: Cold Source And Mini – D2 in SR4 of FRM - 2
For the complete geometric model:
MCNP calculation of spectrum in D$_2$ source
for E > 10 µeV

Calculation of UCN-source in D$_2$

For region of D$_2$-source and connected beam tube or storage: MCNP transport calculation for UCN in D$_2$ and beam tube or storage for 100 neV < E < 252 neV
7. CALCULATION OF SCATTERING LAW DATA $S(\alpha, \beta, T)$ IN ENDF-6 FORMAT AND FURTHER PROCESSING

In Fig. 34 the scheme of generating thermal neutron cross section data sets for a MCNP(X) data library is shown based on the ENDF-6 format and the nuclear data processing system NJOY.

![Diagram](image)

**Figure 34. Neutron Cross Section Processing**

Codes solving the Fourier transformation of the intermediate scattering function for the system neutron-scattering nucleus are LEAPR (solution with the so-called phonon expansion) or GASKET2 (solving by direct integration). In the previous chapters the necessary physical input to these codes as e.g. the generalised frequency distribution $\rho(\omega)$ for solid and liquid moderators was given in detail.

These codes allow to treat frequency distributions composed of free or hindered translations or diffusive motion, a continuous part of a broad band of frequencies (e.g. for hindered rotations) and discrete Einstein $\delta$-oscillators. LEAPR (a module of NJOY) which is from numerical aspects superior to GASKET2, is used to generate the thermal data sets for water and methane as Scattering Law data files $S(\alpha, \beta, T)$ and in addition the elastic scattering part for the solid moderators. These parts are stored in file MF=7 and section MT=4 or MT=2 in the evaluated data file of thermal neutron scattering in moderators.
For fcc Al the incoherent inelastic data set was generated with LEAPR. The coherent elastic file was prepared by our code FCCALPB which was written by Käfer /36/ and then linked with the LEAPR result to the complete ENDF-6 format.

For hydrogen with its free rotations of the molecules both codes are not applicable. At IKE we developed the code SCATHD to handle H\textsubscript{2} or D\textsubscript{2} for solid, liquid or gaseous phases regarding the spin dependent modifications ortho and para. For the liquid phase the static structure factor $S(k)$ considering the intermolecular interference scattering is input for SCATHD. The coherent neutron scattering is handled according to the Vineyard approximation.

With the module THERMR of NJOY thermal scattering cross sections as a function of energy and temperature as well as differential data can be calculated based on the corresponding evaluated thermal neutron scattering file in ENDF/B-6 format. Modifications of the modules LEAPR and THERMR to guarantee a correct processing were necessary and are done at IKE.

The generation of cross section data sets for MCNP(X) from the pointwise files was done by the module ACER.

Two processes are allowed in the $S(\alpha,\beta,T)$ treatment in MCNP(X):

1. inelastic scattering with cross section $\sigma$ (inelastic) and a coupled energy-angle representation derived from the $S(\alpha,\beta,T)$ Scattering Law data in ENDF-6 format
2. elastic scattering with no change in outgoing neutron energy for solids with cross section $\sigma$ (elastic) and an angular treatment derived from lattice parameters.

For inelastic scattering, the secondary energy distributions are represented by a set of equally probable final energies (64) for each member of a grid of initial energies (57) from an upper limit of $\sim$4 eV down to 0.00001 eV along with a set of angular data for each initial and final energy.

8. CONCLUSIONS

For light water for the solid and liquid phases and for hydrogen for the liquid and gaseous phases as well as for solid methane we have derived realistic models to describe the neutron scattering dynamics as a function of energy transfer, impulse change and moderator temperature. The corresponding generalised frequency distributions $\rho(\omega)$ were taken to generate Scattering Law data files in ENDF-6 format for the individual moderator phases for specified temperatures. The code LEAPR of the NJOY code package was used for calculation of $S(\alpha,\beta,T)$ by the so-called phonon expansion method solving the intermediate scattering function. LEAPR was taken to generate the solid and liquid water and methane data sets. The hydrogen data sets were generated with the IKE program SCATHD. For validating of the scattering dynamics models and the calculated Scattering Law data sets $S(\alpha,\beta,T)$ measured differential and integral neutron cross sections were compared with the corresponding calculated ones. It could be shown that the overall agreement of calculated and measured cross sections for all investigated moderators in its different phases generally was very satisfactory.

In addition to the IKE evaluations for the different cold moderators in its special phases we considered other published model assumptions for the neutron-scattering nucleus interaction, took the resulting phonon spectra $\rho(\omega)$ to prepare $S(\alpha,\beta,T)$ files and showed the consequences for calculated neutron scattering cross sections (see e.g. liquid water and solid methane).

For calculation of neutron thermalisation and transport in cold moderators data sets for the neutron transport code MCNP were generated. The data sets can be used with the MCNP versions 4C and X. The content of the prepared MCNP(X) library is described in appendix B.
For the validation of these data sets the calculated neutron flux density spectra for different moderators at two experimental facilities were compared with corresponding measured spectra. Most results agree well within the reported accuracy of measurement. At the present status the generated MCNP library for the moderators ice, water, hydrogen, solid methane, and cold Al as a structure material can be seen as an adequate tool for neutron thermalisation studies in the low temperature range for these moderators. Further validation should be made by application for alternative experiments especially at JESSICA at Jülich. Furthermore, for some moderators like hydrogen new basic data were published recently, which could be used to improve the existing data. For the future, corresponding data for clathrates and further interesting moderator materials (e.g. mesitylene) as well as for mixtures of moderators should be available for extended optimisation of the moderator of pulsed neutron sources.

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Neutron Cross Sections of Cryogenic Materials: A Synthetic Kernel for Molecular Solids

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ABSTRACT

A new synthetic scattering function aimed at the description of the interaction of thermal neutrons with molecular solids has been developed. At low incident neutron energies, both lattice modes and molecular rotations are specifically accounted for, through an expansion of the scattering law in few phonon terms. Simple representations of the molecular dynamical modes are used, in order to produce a fairly accurate description of neutron scattering kernels and cross sections with a minimum set of input data. As the neutron energies become much larger than that corresponding to the characteristic Debye temperature and to the rotational energies of the molecular solid, the ‘phonon formulation’ transforms into the traditional description for molecular gases.

1. INTRODUCTION

With the advent of new projects to build intense neutron sources, and the requirement of copious fluxes of long wavelength neutrons, a revived interest in the development of a new generation of cold neutron sources has prompted an intense wave of efforts all around [1-5]. Obviously, that means improving our present knowledge on existing materials and the development of new ones, in order to achieve higher levels of performance. Most likely, some of those new cryogenic moderators will consist of molecular systems in solid form.

In this work we will discuss a new prescription for the interaction of slow neutrons with molecular solids, to produce the new Synthetic Model for Molecular Solids (SMMS). The basic ideas of this new model were already introduced [6,7], and they are related to previous work done on conventional solids [8]. In essence, our SMMS uses a more realistic description of the dynamics at low energies than the original Synthetic Scattering Function [9], and switches over that formalism at higher neutron energies. Bearing in mind that our primary interest is the description of neutron scattering by cryogenic moderators, most usually composed of hydrogenous molecules, coherent effects are not discussed here.
2. THE CASE OF MOLECULAR SOLIDS

An approximate density of states is used to represent the actual dynamics of the molecular solid:

\[ Z(\omega) = a_s Z_s(\omega) + a_r Z_r(\omega) + a_v Z_v(\omega); \quad a_i \text{ are relative weights.} \]

Under the assumption of no coupling between modes, the intermediate scattering function is

\[ \chi_i(Q,t) = \chi_i(Q,t) \chi_s(Q,t) \chi_v(Q,t) \]

where each of the factors is further assumed to satisfy the Gaussian approximation

\[ \chi_i(Q,t) = \exp \left\{ \frac{\hbar Q^2}{2M_i} a_i [ \gamma_i(t) - \gamma_i(0) ] \right\}; \quad i = s, r, v \]

and the time-dependent mean-square displacement \( \gamma(t) \) is given by

\[ \gamma(t) = \int_0^\infty \frac{Z(\omega)}{\omega} \left[ (n(\omega) + 1)e^{i\omega t} + n(\omega)e^{-i\omega t} \right] d\omega = \sum_i a_i \gamma_i(t) \]

with \( n(\omega) \) being the occupation number. Phonon expansion of the intermediate scattering functions:

\[ \chi_i(Q,t) = e^{-2W_i} \left\{ \sum_m \frac{(2W_i)_m}{m!} \gamma_i(t)^m \gamma_i(0)^{m-1} \right\} \]

where

\[ 2W_i = \frac{\hbar Q^2}{2M_i} \gamma_i(0); \quad \frac{1}{M_i} = \frac{a_i}{M} \]

and the associated scattering laws are given by

\[ S_i(Q,\omega) = e^{-2W_i} \sum_p \frac{(2W_i)_m}{p!} G_p^{(i)}(\omega) \]

\[ G_p^{(i)}(\omega) = \frac{1}{2\pi} \int dt e^{-i\omega t} \left\{ \frac{\gamma_i(t)}{\gamma_i(0)} \right\}^p \]

The complete scattering law is calculated as

\[ S(Q,\omega) = \frac{1}{2\pi\hbar} \int dt \chi(Q,t) e^{-i\omega t} = S_s(Q,\omega) \otimes S_r(Q,\omega) \otimes S_v(Q,\omega) \]

\[ \equiv \exp\left(-2 \sum_{nm} W_{mn} \right) \left[ \delta(h\omega) + S^{\text{inel}}(Q,\omega) \right] \]

The approximated form in the second line is obtained by assuming that the energies of the intramolecular vibrations are too high to be excited either thermally or by collisions under our working conditions (cryogenic temperatures, low incident neutron energies).
To describe the slow-neutron cross sections, we include up to three phonon terms in the inelastic scattering law:

\[
S_{\alpha\beta}^\text{inel}(Q, \omega) \equiv \sum_{p=1}^{3} \frac{(2W_{p})^{p}}{p!} \frac{G_{p}(\omega)}{\hbar} + \sum_{i=1}^{3} \frac{(2W_{i})^{i}}{k!} \frac{G_{i}(\omega)}{\hbar} + \frac{4W_{r}W_{s}}{\hbar^{2}} \left( G_{i}^{(2^*)} \otimes G_{i}^{(2^*)} + W_{r}G_{i}^{(2^*)} \otimes G_{i}^{(2^*)} + W_{k}G_{i}^{(2^*)} \otimes G_{i}^{(2^*)} \right)
\]

where the terms inside curly brackets denote the convolution products of the spectral functions \(G(\omega)\), contributing to processes involving two and three phonons.

**Components of the frequency spectrum**

We introduce here explicit forms for the components of what we call a ‘Synthetic Frequency Spectrum’ (SFS).

**A) Lattice modes**

The dynamics of the solid lattice is represented by the Debye model:

\[
Z_{\omega}(\omega) = 3\omega^{2} / \omega_{D}^{3} \quad (\omega \leq \omega_{D}, \omega = 0 \text{ otherwise})
\]

where the single parameter and the relationship \(\hbar\omega_{D} = k_{B}T_{D}\) denote the Debye frequency \(\omega_{D}\) and temperature \(T_{D}\). Then

\[
\gamma_{i}(t) = \frac{3}{\omega_{D}} \int_{-1}^{1} \tilde{\xi}(x) e^{-i\omega_{D}t} dx
\]

where \(\tilde{\xi}(x) = x / (e^{i\theta} - 1)\) with \(\theta = T / \theta_{D}\). From this

\[
\gamma_{i}(0) = \frac{3}{\omega_{D}} \phi_{i}(\theta),\text{ which defines } \phi_{i}(\theta) \text{ and determines the corresponding Debye-Waller factor:}
\]

\[2W_{r} = \frac{\hbar Q^{2}}{2M_{s}} \frac{3}{\omega_{D}} \phi_{i}(\theta) \quad ; \quad M_{s} = M / a_{s}\]

**B) Rotational modes**

We represent the ‘rotational band’ in the frequency spectrum by:

\[
Z_{\omega}(\omega) = \omega^{2} e^{-\omega / M} / K
\]

a form that satisfies the required behaviour of the frequency distribution in the limit \(\omega \to 0\) [10].

From this representation, we obtain
\[ \gamma_r(0) \equiv \]  
\[ \sigma^2 \left\{ \frac{\pi}{2} \left( \frac{\omega_r}{\sigma} \right) \left[ 1 + \text{erf}\left( \frac{\omega_r}{\sqrt{2}\sigma} \right) \right] + 2 \frac{\omega_r}{\sigma} e^{-\left(\omega_r/2\sigma\right)^2} \left[ 1 + \text{erf}\left( \frac{\omega_r - \sigma^2 / 2\omega_i}{\sqrt{2}\sigma} \right) \right] + e^{-\frac{\omega_r^2}{2\sigma^2}} \right\} / K \]  
where \( \omega_r = kT / \hbar \), \( K \) is the normalization constant, and the Debye-Waller factor for rotations  
\[ 2W_r = \frac{\hbar Q^2}{2M_r} \gamma_r(0); \quad M_r = M / a_r. \]  

C) Vibrational modes

In our description of molecular vibrations, we use the Einstein model to represent those high frequency modes [9]:  
\[ a_r, Z_r(\omega) = \sum_{j} c_j \delta(\omega - \omega_j) \]  
where \( \omega_j \) denotes the eigenfrequency of the \( j \)-th vibrational mode, and \( c_j \) its relative weight.

The width function for this model is:  
\[ \gamma_r(t) = \sum_{j} c_j \omega_j^{-1} \left\{ [n(\omega_j) + 1] e^{i\omega_j t} + n(\omega_j) e^{-i\omega_j t} \right\} \]  
but, under the assumption that \( kT << \hbar \omega_j \forall j \Rightarrow n(\omega_j) \approx 0 \), and then  
\[ \gamma_r(t) = \sum_{j} c_j \omega_j^{-1} e^{i\omega_j t}, \quad \gamma_r(0) = \sum_{j} c_j \omega_j^{-1}. \]  
Finally, the Debye-Waller factor associated to these modes is:  
\[ 2W_r = \frac{\hbar Q^2}{2} \sum_{j} \omega_j^{-1} M_{r,j}, \quad \text{with } M_{r,j} = M / c_j. \]  

Scattering kernels

A) Elastic scattering

The elastic component of the scattering function is given by:  
\[ S^{el}(Q, \omega) = \exp(-2W^{el}) \delta(h\omega) \]  
where  
\[ 2W^{el} = \frac{\hbar Q^2}{2} \left[ \frac{\delta\phi_{\ell}(\theta)}{\omega_0 M_r} + \frac{\gamma_r(0)}{M_r} + \sum_{j} \frac{\omega_j^{-1}}{M_{r,j}} \right] = 2E\Gamma[1 - \cos(\theta)] \]
\[ Q_0 \] denotes the (modulus of) momentum transfer for elastic scattering, \( m \) is the neutron mass, \( \vartheta \) the scattering angle, and

\[
\Gamma = \frac{3\phi(\vartheta)}{\hbar \omega_r A_k} + \frac{\gamma(0)}{\hbar A_k} + \sum_j \left( \frac{\hbar \omega_j}{A_{ij}} \right)^{-1} ; \quad A_k = M_k / m
\]

**B) Inelastic scattering**

The inelastic component of the scattering law according to the present formulation is given by:

\[
S_{\text{inel}}^i(Q, \omega) \equiv e^{-2W_i W_j W_k} \left[ \sum_{p=1}^3 \frac{(2W_i)^p}{p!} \frac{G^{(p)}_{i\omega} \omega_\omega}{\hbar} + \sum_{k=1}^3 \frac{(2W_k)^3}{k!} \frac{G^{(3)}_{k\omega} \omega_\omega}{\hbar} \right]
\]

\[
+ \frac{4W_i W_j W_k}{\hbar^2} \left\{ G^{(3)}_{i\omega} \otimes G^{(1)}_{j\omega} + W_i G^{(1)}_{i\omega} \otimes G^{(1)}_{j\omega} + W_j G^{(1)}_{k\omega} \otimes G^{(1)}_{i\omega} \right\}
\]

where the index '3' reminds us that we are limiting the actual component to a three-phonon expansion.

**3. THE SYNTHETIC MODEL FOR MOLECULAR SOLIDS**

Having introduced an approximate formulation to describe the interaction of slow neutrons with molecular solids, we wish to extend its validity over the complete thermal energy range. This will be our final prescription for a Synthetic Model for Molecular Solids (SMMS), and it will be required to behave as the Synthetic Model for Molecular Gases when the energies involved in the scattering process are much larger than the characteristic Debye energy of the solid lattice. We propose

\[
\sigma^\text{inel} = \left[ 1 - R(E) \right] \left[ \sigma_{SSF} - \sigma^i \right] + \sigma_3
\]

\( R(E) \): a function of the total Debye-Waller factor, with \( R(E \to 0) \to 1, R(E \to \infty) \to 0 \).

For the double-differential cross section, we have

\[
\sigma^\text{inel}(E, E', \vartheta) = \left( \frac{E'}{E} \right)^{1/2} \sum_{i} \left[ \frac{\sigma^i}{4\pi} \right] S^\text{inel}_i(Q, \omega)
\]

with

\[
S^\text{inel}_i(Q, \omega) = \left[ 1 - R(E) \right] \left[ 1 - \sigma^\text{inel}_i(E) / \sigma_{SSF}(E) \right] \Gamma(Q, \omega, E) + S^\text{inel}_i(Q, \omega)
\]

where \( E, E' \), and \( \vartheta \) are the incident, the final neutron energies, and the scattering angle, respectively. As in the case of the original SSF, this pseudo scattering law also depends on the incident neutron energy, \( E \).
4. PRELIMINARY APPLICATION

Solid Methane

It is worth stressing at this point the convenience of modeling separately the different degrees of freedom of a system, including their weights, for a calculational tool devised to tackle situations where complete information on the system is not available. We display in Fig.1 the low energy part of the frequency spectrum for solid methane and its components as defined in Section 1, using a preliminary set of parameters (energies, effective masses). Not shown in Fig.1 but indeed considered in our calculations are the intramolecular vibrations ($\hbar\omega_1 = 0.17$ eV, $\hbar\omega_2 = 0.37$ eV) of the methane molecule, with a total weight of 0.68. We call this complete spectrum the “synthetic frequency spectrum (SFS)”, and it is clear that all available knowledge and expertise should be put together in its construction.

As an example of the synthetic spectrum capabilities, the total scattering cross section of H bound in solid CH$_4$ at 22K is shown in Fig.2 as calculated using the NJOY code, with both the included Harker-Brugger (H-B) spectrum and the proposed SFS for this system.
There is a difference in the inelastic part produced by those evaluations, but the used SFS corresponds to a typical ‘first guess’ in the building of the frequency spectrum for a given system; on the other hand, we are just comparing two calculations here.

We present now specific aspects of our three-phonon algorithm. The families of spectral functions $G(\omega)$, corresponding to ‘lattice’, ‘rotations’ and ‘convolution’ terms in the definition of $S_s^{\omega}(Q,\omega)$ are plotted in Fig.3, for the present case (T = 22K). It is evident the contribution to the scattering law in the small energy-transfer region, caused by $G_{1}^{l}$ that in turn reflects the high population of low-energy rotational modes in solid methane at this temperature.

5. CONCLUSIONS

We have introduced a new synthetic scattering function aimed at the description of the interaction of thermal neutrons with molecular solids. The model is built as a composition of a ‘low’ and a ‘high’ incident energy parts, represented by a phonon expansion of the scattering law for a molecular solid, and the classical form of the Synthetic Model, respectively.

At low incident neutron energies, both lattice modes and molecular rotations are specifically accounted for, through an expansion of the scattering law in few phonon terms. As the neutron energies become much larger than that corresponding to the characteristic Debye temperature and to the rotational energies of the molecular solid, the ‘phonon formulation’ transforms into the traditional description for molecular gases.

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[1] International Workshop on Cold Moderators for Pulsed Neutron Sources (Argonne, USA,1997).


Kinetics of Irradiated Liquid Hydrogen

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ABSTRACT

We present a model for the kinetics of irradiated liquid hydrogen, as appropriate to a spallation neutron source environment. This model indicates that the ortho-para distribution in an irradiated volume of liquid hydrogen may be significantly different from the thermodynamically equilibrated distribution, resulting in significantly changed neutronic and operational performance for practical liquid hydrogen moderators. Numerical experimentation with the model indicates that neither the pulsed nature of a pulsed source nor the cyclic nature of a flowing liquid hydrogen loop significantly impacts the ortho-para distribution. In developing this model, we have learned that many proposed methods for measuring the ortho-para distribution in an operating moderator system may have potential difficulties, complicating benchmarking efforts.

1. INTRODUCTION

Hydrogen at low temperature tends to the para state, with zero molecular angular momentum, in which the proton spins are anti-aligned. This occurs because the spin-zero molecules have accessible the angular momentum-zero state, which has energy about 15 meV lower than the angular momentum-one state, the lowest accessible to the spin-one ortho-molecules. At room temperature, ortho- and parahydrogen molecules exist in the ratio of the numbers of available quantum states, 3:1. This distribution is commonly referred to as \( n-H_2 \), normal hydrogen. Recently-condensed hydrogen slowly approaches the nearly pure para state by spontaneous conversion in which an ortho-hydrogen acts as an agent of spin exchange in either another ortho-hydrogen molecule or in a para-hydrogen molecule. The resulting equilibrated hydrogen is typically referred to as \( e-H_2 \), and for 20.4 K is 0.998 para-hydrogen, and 0.002 ortho-hydrogen. Catalysts in contact with the material hasten the conversion process.

The distinction between ortho- and para-hydrogen is critical in cold neutron source and cold moderator design. [1–4] The peculiarly small total cross section of para-hydrogen for low neutron energies means that low energy neutrons can easily leak out of the medium. Thus the spectral intensity, time response, and overall performance of the moderator in general are very strongly influenced by even small quantities of ortho-hydrogen. Furthermore, different applications (e.g., continuous source, low-resolution pulsed source, high-resolution pulsed source, etc.) may in fact benefit from different ortho:para combinations.

The cold moderator environment necessarily include fluxes of fast neutrons and gamma rays, which dissociate molecular hydrogen. The resulting monatomic hydrogen recombines as though at high temperature, in the 3:1 ortho:para ratio, reversing the relaxation to the para
state. Conversely, the monatomic hydrogen in the presence of ortho-hydrogen molecules may catalyze the relaxation to the para state. Finally, there are indications that a fourth species, triatomic hydrogen, is also present in irradiated hydrogen, presumably resulting from the combination of monohydrogen with ordinary dihydrogen. \cite{5} This trihydrogen is unstable, and can act as a means of “storing” monohydrogen. Thus the ortho:para equilibrium balance in the presence of ionizing radiation may be significantly different from the balance in the absence of radiation. Measurements of the neutronic performance of cold moderators are inconclusive as to the relative concentrations of ortho- and para-hydrogen. \cite{1–4, 6–8}

Our goal is to provide a basis for understanding the evolution of the ortho/para state of liquid hydrogen in the practical circumstance of a radiation environment. Section 2 describes the mathematical models for the kinetics of liquid hydrogen in such a radiation environment. Section 3 applies the model to the Spallation Neutron Source liquid hydrogen moderators, and surveys possible effects of the pulsed nature of source and the circulating nature of the hydrogen loop. Section 4 describes further work we see as necessary.

2. KINETICS MODEL

In an unirradiated liquid hydrogen system, the ortho-para hydrogen distribution can be characterized \cite{9} by

\[
\frac{dn_o}{dt} = K_{po}n_o^2n_{po} - K_{op}n_o^2 + C_{po}n_p - C_{op}n_o,
\]

\[
\frac{dn_p}{dt} = K_{op}n_o^2 - K_{po}n_p n_o + C_{op}n_o - C_{po}n_p.
\]

in which \(n_o\) (\(n_p\)) represents the density of ortho- (para-) hydrogen in the system (we work in units of moles of diatomic hydrogen per cubic centimeter), \(K_{po}\) (\(K_{op}\)) represents the rate constant for ortho-to-para (para-to-ortho) spontaneous spin-exchange conversion, and \(C_{po}\) (\(C_{op}\)) represents the rate constant for ortho-to-para (para-to-ortho) catalyzed conversion. The coefficients are related in that

\[
K_{po} = K_{op}\frac{c_e}{1 - c_e},
\]

as is necessary to reach eventual equilibrium at the ortho-hydrogen fraction

\[
c_e = \left. \frac{n_o}{N_{H_2}} \right|_{t=\infty},
\]

with a similar equation for \(C_{op}\) and \(C_{po}\). Milenko et al. \cite{9} report detailed measurements of ortho-para conversion providing values for \(K_{op}\) as functions of temperature and pressure. The catalytic conversion coefficients will depend completely on the details of the system, such as the material, surface area, and surface preparation of the container, etc., and we consider a broad range of values in our analysis.

Based on the results of irradiation studies conducted in support of the NERVA program, we extend the above mathematical model to include the radiolytic evolution of monatomic and triatomic hydrogen radicals in the hydrogen system, the slow spontaneous dissociation the triatomic hydrogen radicals into additional monatomic hydrogen (and \(e-H_2\)), the ortho-para conversion catalyzing effects of the monatomic hydrogen, and the recombination of the monatomic hydrogen into \(n-H_2\). \cite{10} In mathematical terms, this can be expressed as
where $n_{H_3}(n_H)$ is the molecular density of triatomic (monatomic) hydrogen, and we introduce additional conversion coefficients and parameters as shown in Table 1. We quote values for 20 K and 14.9 bar as typical for cold moderator applications. Obviously, specific systems may have somewhat different values, but they will likely be similar.

### Table 1: Parameters for irradiated hydrogen kinetics model

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Describing</th>
<th>Value at 20 K, 14.9 bar</th>
<th>Source of Value</th>
</tr>
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<tbody>
<tr>
<td>$K_{sp}$</td>
<td>$o$-$H_2$$\rightarrow$$p$-$H_2$ Spontaneous Conversion</td>
<td>$9.54 \times 10^{-5}$ cm$^3$/mole$^s$</td>
<td>Miletinov [9]</td>
</tr>
<tr>
<td>$K_{cp}$</td>
<td>$p$-$H_2$$\rightarrow$$o$-$H_2$ Spontaneous Conversion</td>
<td>As given by $c_e$</td>
<td>Miletinov [9]</td>
</tr>
<tr>
<td>$C_{op}$</td>
<td>$o$-$H_2$$\rightarrow$$p$-$H_2$ Catalyzed Conversion</td>
<td>$0.0 - 1 \times 10^{-2}$ s$^{-1}$</td>
<td>(Variable)</td>
</tr>
<tr>
<td>$C_{po}$</td>
<td>$p$-$H_2$$\rightarrow$$o$-$H_2$ Catalyzed Conversion</td>
<td>As given by $c_e$</td>
<td>(Variable)</td>
</tr>
<tr>
<td>$f_{H_2}$</td>
<td>$H$$\rightarrow$$o$-$H_2$ Recombination Fraction</td>
<td>0.75</td>
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<td>$H$$\rightarrow$$p$-$H_2$ Recombination Fraction</td>
<td>0.25</td>
<td></td>
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<tr>
<td>$f_{H_3}$</td>
<td>$H_3$$\rightarrow$$o$-$H_2$ Dissociation Fraction</td>
<td>$c_e$</td>
<td>Conant [11]</td>
</tr>
<tr>
<td>$f_{H_3}$</td>
<td>$H_3$$\rightarrow$$p$-$H_3$ Dissociation Fraction</td>
<td>$1 - c_e$</td>
<td>Conant [11]</td>
</tr>
<tr>
<td>$K_{H_2}$</td>
<td>$H$$\rightarrow$$H_2$ Recombination Coefficient</td>
<td>$5 \times 10^{-10}$ cm$^3$/mole$^2$/s</td>
<td>Neldn [5]</td>
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<tr>
<td>$G_T$</td>
<td>$o$-$H_2$ and $p$-$H_2$ Radiolytic Destruction</td>
<td>$2.50 \times 10^{-6}$ moles (H$_2$)/J</td>
<td>Neldn [5]</td>
</tr>
<tr>
<td>$G_{H_3}$</td>
<td>$H_2$$\rightarrow$$H_3$ Radiolytic Evolution</td>
<td>$3.42 \times 10^{-7}$ moles (H$_3$)/J</td>
<td>Neldn [5]</td>
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<tr>
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<td>$4.15 \times 10^{-5}$ moles (H)/J</td>
<td>Neldn [5]</td>
</tr>
<tr>
<td>$K_{sp}$</td>
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<td>$8.07 \times 10^{14}$ cm$^3$/mole$^s$</td>
<td>Neldn [5]</td>
</tr>
<tr>
<td>$K_{cp}$</td>
<td>$p$-$H_2$$\rightarrow$$o$-$H_2$ H-catalyzed Conversion</td>
<td>As given by $c_e$</td>
<td>Neldn [5]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$H_3$ Spontaneous Dissociation</td>
<td>$2.06 \times 10^{-3}$ s$^{-1}$</td>
<td>Fessler [12]</td>
</tr>
</tbody>
</table>

### 2.1 Equilibrium Levels

Equation 7 can easily be solved for for the concentration of trihydrogen at equilibrium to give

$$n_{H_3}(\infty) = \frac{G_{H_2}}{\lambda},$$

(9)

giving the result that equilibrium trihydrogen levels are directly proportional to the energy deposition rate. At $E = 1$ W/cm$^3$, the equilibrium level is $1.66 \times 10^{-4}$ moles per cubic centimeter, which implies that $6.7 \times 10^{-3}$ of all hydrogen nuclei are in the trihydrogen species.
Note that the equilibrium trihydrogen level is small enough that for reasonable levels of energy deposition (i.e., 0.02 W/cm³ for SNS) it is neutronically negligible.

Similarly, the approximation that $n_o + n_p \approx N_{H_2}$ with Equation 8 gives

$$n_H(\infty) = \sqrt{\frac{E(G_H + G_{H_2})}{2K_{HH}N_{H_2}}},$$

(10)

giving the result that the equilibrium monohydrogen content is proportional to the square root of the energy deposition rate, and equal to about $1.23 \times 10^{-6}$ moles per cubic centimeter at 1 W/cm³, equivalent to $1.66 \times 10^{-5}$ of all hydrogen nuclei, also neutronically negligible.

3. APPLICATION TO THE SNS MODERATOR SYSTEM

In the SNS environment, we expect that the energy deposition rate in a hydrogen moderator will be as high as 1 W/cm³ in the moderator itself. However, the hydrogen in the moderator rapidly circulates through the rest of the hydrogen loop, where the energy deposition rate is very small. Furthermore, the energy deposition is nearly entirely limited to the first few microseconds following the incident proton pulse. Thus the energy deposition within a volume element of liquid hydrogen circulating through the hydrogen system may be described as having two levels of pulsing; one level on the order of microseconds with a repetition rate corresponding to the source pulsing frequency, and one level on the order of one second (the hydrogen residence time within the moderator) per one minute (corresponding to the circulation time of the hydrogen loop). In our calculations, we use a pulsing frequency of 50 Hz and a loop circulation time of 50 s for numerical convenience. Given an effective residence time of 1 s, the average power density we predict in the SNS hydrogen system is then 0.02 W/cm³.

3.1 Model Results

We first examine the behavior of the model assuming that the energy deposition rate is constant in time, as might apply to a steady-state reactor cold source. The effects of radiation as described in Section 2 result in changed equilibrium levels as indicated in Figure 1. It is immediately evident that radiation energy deposition can radically shift the asymptotic level of ortho-hydrogen in the system, indicating that recombination effects can dominate radiolytic catalysis effects. The hydrogen is not at thermodynamic equilibrium; it is however at an equilibrium between conventional relaxation processes and the back-conversion processes caused by recombination (into $n-H_2$) of radiolytically-produced monohydrogen. Our results indicate that radiation levels depositing 1 W/cm³ can, if system catalysis is small enough, result in a hydrogen makeup comparable to that of freshly-condensed normal hydrogen! For the more modest situation at SNS, we might anticipate steady-state ortho-hydrogen fractions ranging from 0.0021 (almost thermodynamic equilibrium) in the case of very rapid system catalysis, to 0.33 in the case of negligible system catalysis. From this, we can conclude that at reasonable power densities, system catalysis can control the equilibrium level of ortho-hydrogen in an irradiated hydrogen system. As a corollary, if catalysis is not carefully controlled in a high radiation system, the ortho-hydrogen level will be neither controllable nor predictable.

Radiation may also impact the characteristic time for the hydrogen system to approach this shifted equilibrium. Figure 2 shows the time to reach the dynamic equilibrium condition from $n-H_2$, defined as the time at which the ortho-hydrogen concentration is within 10% of its final value (i.e., if the equilibrium ortho-hydrogen concentration is 0.0020, then the time would be defined by when the ortho-hydrogen concentration fell to below 0.0022).
3.2 Model Sensitivity to Source Pulsing and Hydrogen Circulation

Additional studies, not described here, show that the pulsed nature of the energy deposition in a pulsed source moderator does not significantly alter the qualitative behavior of the ortho-
para hydrogen system under irradiation. [13] In the case of either source pulsing or hydrogen circulation in and out of the radiation field, we find that there are relatively small changes in the levels of ortho-hydrogen, and larger changes in the neutronically-insignificant levels of trihydrogen and monohydrogen in the system, and only then at power levels significantly higher than we anticipate in any spallation source or reactor environment.

4. FUTURE WORK

The preliminary nature of this model points the way to significant additional refinements we find necessary. First of all, there is no energy balance condition. Ortho-hydrogen converting to para-hydrogen at 20 K releases some 703 kJ/kg, significantly greater than the latent heat of vaporization (443 kJ/kg). The energy released in this process must be included with other energy source and sink terms in a temperature-dependent refinement to our model. This will introduce significant additional feedback loops to the system. Furthermore, many practical hydrogen systems at neutron sources do involve exchange with a gaseous volume of hydrogen, and the extension of our model to such a two-phase system is very similar to the work done by Nelms and Carter; we anticipate no great difficulty doing so here as well. We do not at the current time foresee a need to make a multi-point model, in which we would consider multiple volume elements of either liquid or gaseous material, but such an extension should be straightforward, if tedious. Further, the parameters and constants used in the model have been assembled from different sources, each of which concerned different efforts done at different times by different groups. An irradiation study conducted specifically to measure the parameters used in this model would likely result in significantly more reliable estimates of the key system parameters. Finally, the most important work we anticipate doing with this model is to test its application to real systems, both currently operating neutron sources (ISIS, the Lujan Center, the NIST reactor) and historical experiments as found in the literature.

5. CONCLUSIONS

Although our model is both limited in its scope and not fully tested, we find that it provides a number of qualitative insights into the likely behavior of liquid hydrogen systems under irradiation. In typical neutron source configurations, our model indicates that

1. irradiation can provide meaningful levels of catalysis for ortho-to-para relaxation,

2. recombination of radiolytically-produced mono-hydrogen can create a dynamic equilibrium level of ortho-hydrogen significantly shifted from the thermodynamic equilibrium level (that is, without radiation),

3. neither trihydrogen nor monohydrogen levels are neutronically significant, and

4. all effects, including those desired from external catalysis, can be considered “averaged over time” in a pulsed source with a flowing hydrogen system where the hydrogen flows out of the neutron field.

These conclusions are qualitative in nature, and will not alter given significant changes in the numerical values of the constants used to analyze the system, or given minor changes in the nature of the kinetics model. In the specific case of the liquid hydrogen moderators at the Spallation Neutron Source, controlling ortho- and para-hydrogen levels is a question of catalysis and power density. The dynamic equilibrium value of the ortho-hydrogen fraction may
be up to 0.30 with low levels of system catalysis, and be nearly identical to thermodynamic equilibrium with high levels of catalysis. Finally, any attempt to measure ortho-hydrogen concentrations in an operating neutron source system must account for the “residual catalyst,” from slowly-decaying trihydrogen, that can cause nearly instantaneous back conversion to higher-temperature-equilibrium ortho-hydrogen levels in the measurement apparatus.

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Composite Hydrogen-Solid Methane Moderators

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ABSTRACT

This paper describes the results of Monte-Carlo calculations for a coupled moderator on a low-power pulsed neutron spallation source and is part of the design study for a second target station for the ISIS spallation source. Various options were compared including hydrogen, solid methane, grooving the solid methane and compound moderators made of hydrogen in front of solid methane. To maximise the neutron current at low energies two strategies appear to emerge from the calculations. For instruments that view a large area of moderator surface a layer of hydrogen in front of a thin solid-methane moderator is optimum, giving a gain of about a factor 10 relative to the current liquid hydrogen moderator on the existing ISIS tantalum target. For instruments that only view a restricted area higher flux, corresponding to a gain of 13.5, can be achieved with the use of a single groove or re-entrant hole in the moderator.

1. INTRODUCTION

This study was carried out in connection with the proposed second target station on the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, in the UK.

The existing target station utilizes a 200 µA, 800MeV proton beam operating at a repetition frequency of 50Hz. The planned extension to the source will involve increasing of the proton current to 300 µA and constructing a second target station, optimized for the production of cold neutrons. One pulse in five will be diverted to the second target station, which will operate at a proton current of 60 µA and a repetition frequency of 10Hz.

The relatively low power (48kW) of the second target station can be put to advantage. In particular, a solid methane moderator, similar to those used on the Intense Pulse Neutron Source at Argonne in the US, would be a practicable alternative to liquid para-hydrogen moderators. However, the problems with the storage of radiation damage in solid-methane and the potential for the explosive release of this energy means that great care has to be taken with the design and operation of solid-methane moderators. With appropriate pre-moderation the heating rate could be reduced sufficiently to enable the moderator to be annealed only once per day.

As currently envisaged, the Second Target Station will include two moderators: a coupled moderator for instruments that are relatively insensitive to pulse widths, and a decoupled moderator for instruments that require short pulse. This paper focuses on design and materials options for the coupled moderator, for which the main optimization criterion is the maximiza-
tion of neutron intensities, particularly in the low-energy range (0 to 5 meV). Pulse widths and time distributions are a secondary consideration, but should be taken into account because they may be important for some instruments. Two moderator materials are considered: liquid para-hydrogen and solid methane, either singly or in combination.

This paper explores two basic options with the aim of significantly improving upon the performance of a simple flat-faced solid methane or liquid hydrogen moderator. The first option involves the use of grooves in solid methane, permitting the instrument to view the cold, intense flux in the moderators’ interior. The second option involves the use of a compound moderator in which solid methane is put behind the hydrogen. The hydrogen compensates for the hardening of the leakage spectrum from the surface of the methane, and the methane compensates for the gap in the hydrogen scattering law at low energies. Above 15 meV the moderator performance and time distributions of the compound moderator are similar to hydrogen. At lower energies the results depend on the hydrogen thickness, a reasonable choice for which is about 5 cm which enhances the neutron intensity by 50% relative to solid methane while producing similar pulse widths.

In Section 2, we discuss the properties of these materials. Solid methane is a typical moderator material, whose total cross-section rises with decreasing energy. However, liquid para-hydrogen is unusual; its neutron cross section is relatively high at energies above the para-ortho transition energy (14.7 meV), but it is comparatively transparent below this energy. This changes the way these materials perform and the way they can be used as moderators.

In section 3, we describe the basic parameters of the Monte-Carlo calculations, including details of the simplified target/moderator/reflector geometry. In sections 4, 5 and 6 we present the results of calculations for flat-faced moderators, multiply grooved moderators and singly grooved moderators respectively. Finally, in section 7 we summarise the overall conclusions of the study.

2. THE PROPERTIES OF SOLID METHANE VERSUS HYDROGEN

The two moderator materials under consideration are liquid hydrogen at approximately 20 K and solid methane, which would in practice be run at about 26-27 K in order to ensure safe operating conditions (the higher the temperature the fewer the annealing cycles). The hydrogen density in the two materials is quite different: approximately 0.076 atoms per barn cm for solid methane but only 0.042 for liquid hydrogen! At neutron energies above about 100 meV this is the most important difference, but atomic binding effects become significant at lower energies. Figure 1 shows the total cross sections for liquid ortho and para-hydrogen and solid methane. The most striking feature of these curves is the unusual behaviour of the para-hydrogen cross section, which almost vanishes below the ortho-
para transition energy. Liquid hydrogen moderators on spallation sources are believed to exist in an almost pure para-hydrogen state, due to the action of powdered magnetic catalysts in the cooling circuit, and are therefore relatively transparent to neutrons below 15meV (although it should be noted that a small proportion of ortho-hydrogen would significantly increase the neutron cross section in this energy range). The low-energy properties of liquid para-hydrogen are in fact highly advantageous. The rapid release of sub-15meV neutrons from the moderator produces relatively sharp time distributions and high levels of neutron leakage in this energy range, although the leakage drops away at lower energies.

Both moderators have advantages and disadvantages: solid methane is an excellent moderator, but the neutron's mean free path is very short at low energies so the optimum width is narrow (2 to 3cm). Making the moderator thicker means that you get larger flux at its centre, but does not increase the surface leakage.

3. THE DETAILS OF THE CALCULATIONS

All the calculations were carried out using the Monte-Carlo code MCNPX [1], which is a new version of MCNP[2] which incorporates the capabilities of LAHET[3] into the MCNP code, thus permitting the calculation to include high-energy charged particles (e.g. protons, pions) as well as neutrons, photons and electrons.

The geometry used is illustrated in Figure 2. This is a highly simplified version of the currently envisaged geometry for the proposed ISIS Second Target Station. The reflector is an 80cm cube of heavy-water cooled beryllium, represented by a homogenized mixture (20% D₂O, 80% Be by volume). The target is a tungsten cylinder of diameter 6cm, surrounded by a 10cm square cell containing light water (with the dual function of cooling the target and pre-moderating the neutron spectrum to reduce the heat load on the solid methane moderators to acceptable levels). The source was a proton beam of energy 800MeV and current 60µA. The beam diameter was 3cm, and the radial intensity profile was a Gaussian with σ = 0.5cm and a 3σ cut-off. Only one moderator was included in the configuration. This was placed above the target in ‘wing’ geometry, with beam ports on both sides. The thickness and composition of the moderator...
varied between calculations but the transverse dimensions were always $12 \times 12$ cm$^2$.

The thermal neutron cross-section kernels [4] used in this study were those made available to participants in the Cold Moderator study. Documentation on the methods used to describe the kernels is given in Ref. [5].

Two methods were used for the tallying of the neutron current at the moderator surface. The time-integrated current was obtained, for a direction orthogonal to the moderator surface, using a distant point detector. The time distribution of the current was obtained using a surface-crossing tally, but the time-dependent leakage was normalized to produce the time-integrated values determined by the point detector.

4. THE OPTIMISATION OF THE FLAT FACE MODERATORS

Three series of calculations were carried out:

(i) Solid methane moderators of variable thickness (in 1 cm steps up to 6 cm), tallies scored for both faces.

(ii) Liquid hydrogen moderators of variable thickness (in 1.6 cm steps up to 9.6 cm), tallies scored for both faces.

(iii) Composite moderators consisting of a hydrogen moderator in front of a methane moderator. Tallies were scored for the hydrogen face only.

Table 7. The time-integrated intensities in the 0-5 meV energy range. The results are given relative to a 4.8 cm thick liquid hydrogen moderator. The lateral dimensions of the moderator are 12 x 12 cm, and the temperatures are 26 K and 20 K for the solid methane and hydrogen respectively. The error in the last significant figure is shown in brackets. The time integration is from 0 to 30,000 µs.

<table>
<thead>
<tr>
<th>Hydrogen thickness (cm)</th>
<th>Methane thickness (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>1.140(5)</td>
</tr>
<tr>
<td>2</td>
<td>1.351(6)</td>
</tr>
<tr>
<td>3</td>
<td>1.326(6)</td>
</tr>
<tr>
<td>4</td>
<td>1.285(6)</td>
</tr>
<tr>
<td>5</td>
<td>1.241(6)</td>
</tr>
<tr>
<td>6</td>
<td>1.214(6)</td>
</tr>
</tbody>
</table>

The results for time-integrated leakage are shown in Table 7. All values are given relative to a reference case: 4.8 cm hydrogen. It is interesting to compare the non-composite hydrogen and methane moderators. The methane moderator has an optimum thickness of between 2 cm and 3 cm, whereas the hydrogen moderator continues to give a better performance as its thickness is increased. However, it is clear that the composite moderator show a significant performance enhancement relative to non-composite moderators at energies below 15 meV.

Figure 3 shows the calculated FWHM pulse widths for non-composite moderators and for composite moderators with 2 cm methane. The pulse widths from methane are largely independent of thickness, whereas, at low energies, the hydrogen pulse widths rise. However, the hydrogen moderator still gives sharper pulses than the methane for thicknesses of less than 10 cm, albeit with a flux penalty.
The results for the composite moderator are more complex; with a switch between different behaviours above and below 15 meV. At low energies the pulse width get narrower when a thin layer of hydrogen is added, but the addition of further hydrogen significantly increases the pulse widths as well as increasing the neutron leakage. At higher energies, the moderator starts looking like a methane moderator but becomes more hydrogen like as the hydrogen thickness increases. A good compromise would be about 2 cm methane with 5 cm hydrogen, giving a pulse width about the same as the pure methane moderator but with a performance gain of over 2 relative to 4.8 cm hydrogen and 50% better than 2 cm methane alone.

Figure 4 shows the time distributions from 4.8 cm and 6.4 cm hydrogen moderators, and for some of the cases with 2 cm solid methane. It is clear that increases in the hydrogen thickness also increase the pulse width, but the bulk of the increase lies within the pulse; there is no large increase in the tail. The composite moderator shows that increasing the amount of hydrogen increases both pulse width and height with no detrimental effect on the tail.

![Figure 3. Plots of the FWHM pulse widths versus the moderator thickness, for both the flat face moderators, in all four of the calculated energy ranges.](image1)

![Figure 4. The pulse shapes for the 0 to 5 meV energy group for some of the simple and composite moderators flat face moderators.](image2)
5. THE OPTIMISATION OF MULTIPLY GROOVED MODERATORS

One of the common ways to improve the flux from solid methane is to add a series of narrow grooves into the moderator. This presents us with a huge parameter space to study, so we have selected a few key points in this space to give us an idea about the possible performance. For the purposes of this study, we have added four horizontal grooves (Figure 5). In the initial configuration, the grooves extended half way into the moderator; the groove height was specified as 1.5 cm, with 1.5 cm of solid methane between the grooves. However, the enlargement of the grooves was found to be desirable, and later calculations used 2cm grooves separated by 1cm of moderator material. Similarly, the extension of the grooves further into the moderator proved to be advantageous, and later calculations all used grooves whose depth was 2/3 of the moderator thickness.

Two options for the use of para-hydrogen in conjunction with a grooved methane moderator were explored: adding hydrogen inside the grooves, and/or an additional flat-faced hydrogen moderator in front of the grooves.

Results for the time-integrated current are shown in Table 8 for selected cases. The best results appear to be from the case with hydrogen in front of empty grooves. However, this is only the case if the time integration is taken over the whole of the long tail. A more careful look at the peak shapes (figure 7) shows that for empty grooves the shape is double peaked and that adding hydrogen to the grooves adds height to the peak and produces a clean single shape with 10% extra flux in the 0 to 2000 µs region. Controlling the long time tail is obviously something that needs to be addressed, perhaps by adding a poisoning layer deep in the reflector.

In Figure 6 the FWHM of these selected cases is shown as a function of thickness. One of the remarkable results is how the addition of hydrogen into the grooves sharpens up the pulse. From Figure 7 we can see that above 200µs the peak shapes for hydrogen in front of empty grooves and grooves filled with hydrogen are roughly the same (although the empty grooves are very slightly higher), but below 200µs there is a higher, sharper peak.

![Figure 5. The geometry of the multiply grooved moderators (vertical section). The moderator has lateral dimensions of 12 x 12 cm with four horizontal grooves. Various geometries have been run with different groove widths, separations and depths. Compound moderators incorporating a slab of hydrogen moderator in front of the grooves were also investigated.](image-url)
Table 8: A summary of calculated neutron intensities from multiply grooved moderators. The results are given relative to a 4.8cm flat-faced liquid hydrogen moderator. The lateral dimensions are 12 x 12 cm and the temperatures are 26K and 20K for the solid methane and hydrogen respectively. The time integration is from 0 to 30,000µs.

<table>
<thead>
<tr>
<th>Methane thickness (cm)</th>
<th>Hydrogen thickness (cm)</th>
<th>Height (cm)</th>
<th>Fractional depth</th>
<th>Groove material</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>0.0</td>
<td>1.5</td>
<td>1.5</td>
<td>0.5</td>
<td>void</td>
</tr>
<tr>
<td>8.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
<td>void</td>
</tr>
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<td>1.5</td>
<td>0.67</td>
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</tr>
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<td>void</td>
</tr>
<tr>
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<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
<td>void</td>
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<td>1.0</td>
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<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
<td>void</td>
</tr>
<tr>
<td>8.0</td>
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<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
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</tr>
<tr>
<td>10.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
<td>void</td>
</tr>
<tr>
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<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>void</td>
</tr>
<tr>
<td>4.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>void</td>
</tr>
<tr>
<td>6.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>void</td>
</tr>
<tr>
<td>8.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>void</td>
</tr>
<tr>
<td>10.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>void</td>
</tr>
<tr>
<td>2.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
<tr>
<td>4.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
<tr>
<td>6.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
<tr>
<td>8.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
<tr>
<td>10.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
<tr>
<td>6.0</td>
<td>1.6</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
<tr>
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<td>3.2</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
<tr>
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<td>4.8</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
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<td>1.6</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
<tr>
<td>6.0</td>
<td>3.2</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
<tr>
<td>6.0</td>
<td>4.8</td>
<td>2.0</td>
<td>1.0</td>
<td>0.67</td>
<td>H₂</td>
</tr>
</tbody>
</table>

Figure 6. Plots of the FWHM pulse widths versus the moderator thickness for the multiply grooved moderators. There are four grooves, each 2cm high and separated by 1cm of solid methane. The methane moderator is 6cm thick with grooves 4cm deep and has lateral dimensions 12x12 cm.
6. SINGLE GROOVE CALCULATIONS

Some neutron instruments, such as small angle or reflection machines only view a restricted area of the moderator face. This makes it possible to either use a large single groove or re-entrant hole in the moderator, which offers the prospect of larger gains than either the flat face or multiply grooved moderators.

Figure 8 shows the geometry of the single-groove moderator, the design of which had been optimized in previous studies. A tapered slot of height 4cm, depth 6.5 cm and width 8.4 cm (at rear) is cut into a moderator of dimensions 10 cm (height), 16 cm (width), 11 cm (depth).

The results for the time-integrated neutron current (again normalized to a simple 4.8cm hydrogen moderator) and pulse widths can be seen in table 3. The 0 to 5meV energy group shows a gain of approximately 2.7 relative to a simple 4.8cm hydrogen slab, and represents a significant improvement on the compound and multiply-grooved cases. However, it should be noted that the performance of the single-groove moderator is inferior to the flat-faced and multiply grooved moderators at energies above 5meV.

Figure 9 shows the calculated time distributions in the 0 to 5meV energy group, compared with the optimal compound-moderator case (4.8cm liquid hydrogen in front of 2cm solid methane). The grooved moderator produces a somewhat longer pulse width than the compound flat-faced moderator. However, it is evident that the gain from the grooved versus
the flat-faced moderator is ‘real’ in the sense that the bulk of the increased neutron flux occurs near the peak and not in the long-time tail.

Table 2. Calculated neutron intensities and pulse widths for the single-groove moderator.

<table>
<thead>
<tr>
<th>Group (meV)</th>
<th>Relative Intensity</th>
<th>FWHM of pulse (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 5</td>
<td>2.70(1)</td>
<td>251(8)</td>
</tr>
<tr>
<td>5 - 15</td>
<td>1.281(9)</td>
<td>70(4)</td>
</tr>
<tr>
<td>15 - 30</td>
<td>0.618(6)</td>
<td>11.5(8)</td>
</tr>
<tr>
<td>30 - 100</td>
<td>1.02(1)</td>
<td>7.6(5)</td>
</tr>
</tbody>
</table>

7. DISCUSSION

Except where otherwise stated, the following discussion will focus on the moderator performance in the 0 to 5meV energy group relative to a simple 12 x 12 x 4.8cm³ liquid hydrogen moderator.

In the case of the flat-faced compound moderators; good results were obtained using a liquid hydrogen moderator in front of a 2cm thick solid methane moderator. The performance increased with the thickness of the hydrogen moderator, at the expense of increasing pulse widths. Our design brief for the coupled moderator was for the highest possible intensity at low energies. The moderator which best fits this brief is the combination of 2cm of solid methane and 4.8cm of hydrogen; giving a performance gain of 2.06 relative to a simple 4.8 cm hydrogen slab.

The concept of a multiply grooved methane moderator also proved highly successful. From the point of view of maximizing neutron intensity, the best arrangement proved to be a...
4.8 cm hydrogen slab in front of a 6cm grooved methane moderator (groove depth 4 cm, height 2 cm, separation between grooves 1cm, no material in the grooves). Flowing hydrogen into the grooves produced significantly 'cleaner' and sharper pulses. The best compromise is a 3.2 cm hydrogen moderator in front of a 6cm solid methane moderator (grooves as described above but containing hydrogen), which would give a gain of 2.05 relative to a simple slab. Given that this gain is very similar to that for the simpler flat face design it is unlikely that this will be chosen in reality.

The results for a single-groove moderator were good, the optimum result being a gain of 2.70 relative to a simple 4.8 cm hydrogen slab. This would provide a substantial performance enhancement for cold-neutron (< 5 meV) for instruments which view a limited section (~4 cm) of the moderator height.

It is interesting to compare the results with the liquid hydrogen moderator on the existing ISIS target (on the basis of flux per MW of beam power.) In the case of the flat-faced moderator (4.8cm hydrogen, 2cm solid methane), the calculated gain relative to the liquid hydrogen moderator on ISIS is 20.7 and the gain for the single groove moderator is 27.0. These gains sound very large but two points should be remembered:

a) The hydrogen moderator on the existing target is decoupled.

b) These gains are exaggerated by the omission of significant system components (moderator cans, target pressure vessel and cooling manifold) from the simplified model used in this paper. Later calculations in a more realistic geometry have shown that the simplified geometry provides accurate estimates of relative moderator performance, but over-predicts the absolute fluxes by about a factor of two; thus the true gains for the flat-faced and singly grooved moderators are 10 and 13.5 respectively.

7.1 The optimum moderator for instruments view the whole moderator

The optimum cases for the flat-faced and multiply grooved compound moderators give almost identical performance for the time-integrated neutron current. However, the flat-faced configuration is considered superior to the multiply grooved case for three reasons:

a) The flat-faced moderator gives a sharper pulse (FWHM 231 µs) compared with the grooved case (FWHM 291 µs).

b) Given that the flux gains are similar, the extra engineering complexity of the multiply grooved moderator does not appear to be warranted.

Table 4 summarizes the pulse widths and moderator performance for a 5 + 2 + 5 cm sandwich as described above, compared with the 4.8 + 2 cm flat-faced compound moderator. The sandwich produces almost identical time distributions to the two-part compound moderator, but there is a small penalty of about 7% in the time-integrated intensity.
7.2 The optimum moderator for instrument that view a restricted area of the moderator

Table 5 summarizes the pulse widths and moderator performance for a modified version of the single-groove moderator, in which 2cm of solid methane is removed from the flat face and replaced with 4cm of liquid hydrogen. This design successfully combines the performance of both the single-groove and flat-faced moderators. This will allow those instruments that can to take advantage of the high flux from the groove, but also have a high flux face available for those instruments that require a view of the full moderator height. This design has been adopted as the basis for future studies.

<table>
<thead>
<tr>
<th>Energy Range (meV)</th>
<th>Relative Intensity</th>
<th>FWHM of pulse(µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Grooved face</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 - 5</td>
<td>2.65(2)</td>
<td>241(7)</td>
</tr>
<tr>
<td>5 - 15</td>
<td>1.264(8)</td>
<td>64(3)</td>
</tr>
<tr>
<td>15 - 30</td>
<td>0.623(6)</td>
<td>11.4(8)</td>
</tr>
<tr>
<td>30 - 100</td>
<td>1.04(1)</td>
<td>7.7(5)</td>
</tr>
<tr>
<td><strong>Compound flat face</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 - 5</td>
<td>1.95(1)</td>
<td>209(3)</td>
</tr>
<tr>
<td>5 - 15</td>
<td>1.345(7)</td>
<td>83(2)</td>
</tr>
<tr>
<td>15 - 30</td>
<td>0.754(5)</td>
<td>35(1)</td>
</tr>
<tr>
<td>30 - 100</td>
<td>0.780(8)</td>
<td>13.2(4)</td>
</tr>
</tbody>
</table>

Table 5: Summary of the neutron intensities and pulse widths from a single groove moderator with a compound flat face.

8. REFERENCES


[4] McFarlane et al., private communication. (Data available to participants of the Cold Moderator Collaboration. For details contact rym@lanl.gov.)

Automation Techniques applied to systematic studies of moderator coupling

S. Ansell, J.F. Garcia, S.M. Bennington, D.J. Picton, T. Broome
Rutherford Appleton Lab, Chilton, UK

ABSTRACT

We present new computation methods in which the geometry management of MCNPX input files can be automated. We demonstrate this method with respect to the target station 2 design at ISIS. The method presented is not a mathematically robust method, but by starting from a valid baseline model allows this model to be mutated in a reliable way. Those features that still need to be improved and added are discussed at the end. We use this method to show that a mixed lead/water pre-moderator gives a better neutron flux to radiation damage ratio for the coupled moderator.

1. INTRODUCTION

The ISIS second target station is required to deliver high brilliance, long wavelength neutrons to a wide range of instruments. The existing synchrotron will deliver protons to the target at 800MeV with a 10Hz frequency. This low power from the proton beam allows a solid target design and a full range of cryogenic moderators to be used without excessive engineering complexity.

The design of the moderators is being carried out using neutronic Monte Carlo simulations to optimize different design parameters. These simulations do not differ significantly in their information content and accuracy of the Monte Carlo results, relative to previous design work on other moderator assemblies. However, the dramatic increase in computing power means that the simulations can search a parameter space with a realistic engineering description. This allows the effect of vacuum gaps, composite materials, pipe work and mounting points to be incorporated.

The current simulations were carried out on a 32 node Beowulf cluster of 1.6GHz CPUs with an ethernet backplane. The simulation code was MCNPX version 2.2.5 beta release. For a typical model, this allows 450 runs/day with a 1% tally accuracy for a typical plot of energy vs intensity. This level of computing power shows the essential requirement that the job submission, optimization and result reporting is automated.

We have developed a new suite of automated software for these types of problems and we will highlight the capabilities by means of an example. The coupled moderator of target station 2 is a high intensity, broad pulse shape moderator. The objective is to maximize the flux over a large wavelength range without regard to the time structure. Therefore, the coupled moderator has been designed with a basic figure of merit (F.o.M.) expressed as

$$F_{o\cdot M} = \int_{0.1}^{20} I(\lambda)\lambda^2 d\lambda$$

The basic components of the coupled moderator (Figure 1) are the solid cylindrical tungsten target, which is cooled by a layer of D$_2$O, contained in a steel pressure vessel. The thickness of the steel and D$_2$O layers has been determined by the engineering constraints
rather than neutronic considerations and cannot be altered. The target radius had previously been optimized by maximizing the neutron flux (below 5MeV) on the outer surface of the steel pressure vessel.

Figure 1. The layout of the groove moderator, showing a water pre-moderator. The hydrogen layer does not need such a large pre-moderator so a void has been left.

Above the target is the pre-moderator of room temperature H₂O which acts to localize the fast neutrons near the moderator. It has an additional function in reducing the heat load on the moderator. The cryogenic part of the moderator sits directly on top of the pre-moderator. The coupled moderator consists of two sides, one is a solid methane block in which a 3x8cm² groove has been cut out. The instruments on this side only view the centre of the groove, and obtain a high neutron flux. The grooved side is considered as the primary face and all optimizations are to maximize the F.o.M. from this face. The other side is a block of liquid hydrogen, which is viewed by those requiring the highest number of neutrons possible due to its larger surface area, although not at the same flux density of the grooved face.

In addition to maximizing the F.o.M. for the neutron flux, it is also necessary to consider the heating of the moderator. The heat tally is used for two purposes (i) to estimate the cooling power required by the cryogenic system, (ii) to estimate the radiation damage to the solid methane. In the second case we assume that the heating power is proportional to the radiation damage sustained. We can compare the heating power results from our model to the heating power obtained with the IPNS MCNPX model, and extrapolate to the actual radiation damage observed at the IPNS. The IPNS uses a 15µAmp beam on their current solid methane moderators and requires an anneal every 3 days. For the TS2 design study, it is proposed that
the moderator is annealed every 12 hours. This results in us requiring a peak heating power of 0.08W/cc at 60µAmp.

In the TS2 design, the optimal neutronic pre-moderator would be a 1.2cm thick H₂O slab, in order to obtain the maximum F.o.M. However, when the radiation damage to the moderator is considered, a 3.4cm thick pre-moderator would be required in order to obtain an appropriate anneal time. This results in a 35% loss in the F.o.M.

There are several possible optimization points for maintaining the heating power, whilst increasing the neutron flux. This is because about 30% of the radiation damage comes from gamma-ray produced in the target. The neutron yield from the target surface is peaked at 4.5cm from the front face of the target, whilst the gamma yield is peaked at 6cm, and falls off considerably less rapidly than the neutron production. The gamma ray heating component can then be isolated from the moderator by using a suitable shielding material, that allows the neutrons through, or geometrically by suppressing the gamma ray flux from the back of the target.

The first candidate for gamma shielding is the target material itself. If the target radius is increased, the target acts to shield its own gamma production whilst increasing the number of (n,xn) reactions. However, this has the effect of increasing the moderator to target distance and increasing the volume of steel and coolant D₂O used. This is because the thickness of coolant and steel must be maintained. It also does not allow separate optimization of the hydrogen and CH₄ pre-moderators.

A second candidate solution is to use a lead layer in the pre-moderator to suppress gamma rays coming from the target. It allows the lead to be specifically tailored to the incoming gamma ray flux and the hot spots within the CH₄ moderator since it is only the peak heating power that must be kept below 0.08W/cc.

2. OPTIMIZATION METHODS

In order to determine the optimal configuration, we decided to optimize both candidate models at the same time. We allowed both the radius of the target to vary and the thickness of the lead layer including allowing the lead layer to have zero thickness. The procedure to solve this optimization problem was as follows:

i. Set the radius and the thickness of the lead
ii. Run MCNPX models, adjusting the pre-moderator thickness until the peak heating power was optimized to 0.08W/cc
iii. Make a long run of MCNPX
iv. Calculate the flux and F.o.M. from the moderator
v. Based on the F.o.M. obtained, adjust the radius and lead thickness again
vi. Repeat from 2

This procedure requires a considerable degree of sophistication in the job control scripts for which the minimum features are: (i) the control script must be able to write a valid MCNPX input deck, (ii) the script must be able to add/remove tallies, (iii) it must be able to make geometric adjustments to many different components within the system, (iv) the script must be able to determine when a job has finished and (v) the tallies and F.o.M.'s must be calculated and their errors assessed.

The most difficult part of the above procedure is to maintain the geometric integrity. This is made significantly more difficult by the MCNPX requirement that each shape is both internally and externally defined by its bounding surfaces. There are highly developed methodologies based on the point bound region approach to 3D geometric definitions.
However, this cannot be used in MCNPX because the run time penalty for using such a description is too high. Instead, we have developed a geometric control mechanism to allow adjustments to an surface defined set of objects.

3. GEOMETRIC CONTROL

The geometric control system works by defining objects in three classes: user defined, mutable and filler, and by working with a default geometric configuration. This baseline arrangement must be a valid MCNPX input geometry in which there are no overlapping object or void volumes.

3.1 User Defined Objects

The user defined object refers to those components that the user fitting algorithm wishes to directly control, e.g. the pre-moderator r the target shape. They are the simplest objects since they have only to be parameterised and positioned within the final model. They re the first objects placed into the model. After all user objects have been inserted, a simple check is made to see if any of the vertices of each object lie within another object. This check is not a rigorous overlapping check but due to the nature of most MCNPX problems, it is normally sufficient. A full check would require that the smallest distance between two vertices on one object is calculated and then that each external line of each object is divided into points separated by this minimum distance. If none of these points were found to be within another object then this would be sufficient proof that no objects overlap. However, the weaker but significantly quicker method has been used throughout. In the event of an overlap occurring, this will be picked up when MCNPX loses particle tracks, however, this will terminate the optimisation run.

3.2 Mutable Objects

The mutable objects are objects that cannot be completely allowed to absorb the changes to the user defined object. For example, the aluminium can surrounding the pre-moderator should retain its thickness, as the pre-moderator is changed. The process of generating the final position of the mutable object is carried out using an iterative procedure.

i. Calculate the external convex hull of the mutable object
ii. Determine if any user objects reside completely within this convex hull
iii. If yes, determine the modification required to the mutable object and repeat from 1 for all mutable objects
iv. While mutable objects exist repeat from 1
v. Calculate all interactions that are common, i.e. two objects which wish to move a common surface in two different directions and resolve the conflict
vi. Loop over all mutable objects in inclusion order
vii. Calculate shared surface between the mutable and user objects
viii. If the shared surface has moved, displace the mutable object and all objects within it.

The inclusion order is defined as the order of objects based on the number of object layers contained within its convex hull. Single objects with no included objects come higher up the list than objects containing an included object. Objects which have multiple shells, e.g. A includes B, and B includes C, are placed lower. The list is further resolved by promoting those objects which encase a smaller volume.
The method requires two additional algorithms, one for resolving the case where an object contains another object and the second for resolving the case when an object impinges into a neighbouring object.

The containment algorithm is a simplified version of the minimum enclosure method [1]. First, the surfaces of the convex hull surrounding the inner object are calculated. Then the displacement of these surfaces relative to the baseline shape and position of original convex hull surfaces is calculated. Next, for each true surface of the enclosing object (this includes all internal and concave external surfaces), project the normal of the plane from the surface centre and each vertex of this true surface towards the inner convex hull. The normal of the plane surface \( n_{\text{Hull}} \) on the inner convex hull at which the incoming vector intersects is determined. The maximum value of \( n_{\text{surface}} \cdot n_{\text{Hull}} \) is found and the outer surface is displaced by \( D_{\text{Hull}} \), where \( D_{\text{Hull}} \) is the distance the intersected surface moved relative to its baseline position.

This algorithm is not infallible but deals with 90% of the object interactions.

The interference algorithm is based on calculating the extent to which the incident object overlapped the secondary object and moving the secondary object to reduce the overlap to zero. If this cannot be achieved an error is generated for user intervention. First, the overlap of the convex hulls in the original baseline model is calculated. This is not always zero because objects can interlock with a concave intersection that the convex hull does not contain. Second, the overlapping intersectional volume of the two convex hulls is calculated and the centre of the mass for the overlapping volume is computed. Third, the overlapping intersection is calculated for a slightly smaller movement of the incident object, and the centre of mass of this intersecting component is calculated. The two centres of mass then form the vector along which the secondary object is moved, until it does not overlap.

This method is not completely reliable and a history of each object is required to be stored, but it is simple to implement.

3.3 Filler Objects

Filler objects do not have any mutation under the current system. They will be expanded or contracted as other objects move. The only exception to this has been the flight lines which have had their horizontal planes tracked to the centres of the moderator faces.

There are a number of difficulties with the current implementation. The code was written in Python, and runs very slowly. This is particularly apparent for objects with large number of surfaces, when the number of vertices increases at the rate \( N(N-1)(N-2) \) and thus can be very large for even moderately sized objects.

4. RESULTS

The method has been applied to the problem of increasing the flux of the moderator by decreasing the heat-load associated with gamma rays. Simulations were carried out and the results are presented in table 1.

<table>
<thead>
<tr>
<th>Parameters varied</th>
<th>Best Values</th>
<th>Gain in Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius</td>
<td>3.9cm</td>
<td>10%</td>
</tr>
<tr>
<td>Lead</td>
<td>1.9cm</td>
<td>8%</td>
</tr>
<tr>
<td>Radius + Lead</td>
<td>Radius = 3.3cm and Pb=0.7cm</td>
<td>14%</td>
</tr>
</tbody>
</table>

Table 1. Results from the runs using the multi-parameter fitting method.
The results show the system of multiple parameter optimization can be beneficial. The advantage of the current system is that the whole flight-lines and moderator are required to move as the pre-moderator is changed and this saves significant human effort. It is the ability to move a large number of objects coherently that allows models with significant amount of engineering detail to be optimized.

5. CONCLUSIONS

We have a first version of a geometry handling package for MCNPX simulations. It can be used to refine a geometry without direct configuration of the components. This shows promise to allow optimization of significantly more complex models than are currently parameterised.

REFERENCES


ACKNOWLEDGEMENTS

The authors wish to acknowledge the invaluable help provided by D. Picton on problems with MCNPX.
ABSTRACT

The objective of this study was to examine the flow behavior of a methane hydrate/methane-liquid hydrogen dispersed two-phase fluid through a given design of a moderator chamber for the ESS target system. The calculations under simplified conditions, e.g., taking no account of heat input from outside, have shown that the computer code used, CFX, was able to simulate the behavior of the two-phase flow through the moderator chamber, producing reasonable results up to a certain level of the solid phase fraction, that allowed a continuous flow process through the chamber. Inlet flows with larger solid phase fractions than 40 vol% were found to be a "problem" for the computer code. From the computer runs based on fractions between 20 and 40 vol%, it was observed that with increasing solid phase fraction at the inlet, the resulting flow pattern revealed a strong tendency for blockage within the chamber, supported by the “heavy weight” of the pellets compared to the carrying liquid. Locations which are prone to the development of such uneven flow behavior are the areas around the turning points in the semispheres and near the exit of the moderator. The considered moderator chamber with horizontal inlet and outlet flow for a solid-liquid two-phase fluid does not seem to be an appropriate design.

1. INTRODUCTION

Both hydrogen and methane are currently being widely applied as cryogenic moderator material in target systems of neutron sources. Supercritical hydrogen is the material of choice for the reference design of the European Spallation Source (ESS) cryogenic moderator, as has also been selected for the US spallation source SNS as well as for the respective Japanese project SNS.

Solid methane as moderator material, which is also in use in different facilities, is known to outperform liquid hydrogen in terms of neutronic characteristics. It is, however, not appropriate for higher power neutron sources such as the ESS because of its radiation-induced decomposition, where exothermal recombination processes of the radicals represent a significant risk.

In order to combine the advantages of both materials and mitigate their drawbacks, a mixed moderator concept of solid methane pellets plus liquid hydrogen (LH₂) has been proposed first by Lukas in 1988 [1], which is expected to provide a high cold neutron intensity and narrow pulses of thermal neutrons and to operate also at higher powers.

The aim of the study here is the computer simulation of the flow behavior of the above mentioned solid-liquid two-phase system within the moderator chamber as presently designed for the ESS facility. The calculational tool is a Computer Fluid Dynamics (CFD) code, which is principally able to handle multi-phase flows in complex geometries. Multi-phase flow refers to a situation where more than one fluid, not necessarily different phases of the same species, may be present. Unlike multi-component systems, multi-phase flows consist of species which are mixed at much larger than molecular scale. All phases will potentially have differ-
ent velocities and temperature fields interacting empirically specified inter-phase transfer terms. In the case presented here, a disperse two-phase flow, i.e. the flow of a disperse phase (particles) in a continuous phase (gas, liquid) is treated.

2. THEORETICAL STUDY OF A LIQUID-PARTICLE FLOW IN THE ESS CRYOGENIC MODERATOR

2.1. Calculational Tool

State-of-the-art modeling of the transient behavior of a fluid is given by computer fluid dynamics (CFD) models which simulate complex flow processes by solving the Navier-Stokes equations in a three-dimensional calculation grid structure. This approach comprises the conservation equations of mass, momentum, and energy. In the two-equation k-ε turbulence model, special partial differential equations are solved to describe the transport of turbulence as well as its generation and dissipation. Of all the approaches, the k-ε model offers the highest relative independence of empirical relations.

The commercially available CFD code “CFX” by AEA Technology [2] has been applied for this study. By means of a specific command language, the user determines the numerical parameters and the case-dependent physical models. The code allows the construction of a body-fitted calculation grid. The multi-block structure of the grid enables local refinement where desired or requested. Among various robust advanced methods of a numerical solution procedure, the most appropriate for the case considered can be selected (by experience or by trial and error).

The physical models offered are valid for either steady state or transient conditions. Apart from the models for heat transfer by convection, conduction, or radiation, the models include multi-phase flow as well as phase changes and chemical reactions, covering also the simulation of fire and explosion, which may be applied in follow-on studies.

Regarding the two-phase flow, as is applied in this study, both phases are assumed to be present in each control volume and assigned a respective volume fraction (“inter-penetrating continuum”). Restrictions to the model are:

(a) The multi-phase flow is assumed incompressible or weakly compressible.
(b) No radiation heat transfer is allowed.
(c) All phases must use the same turbulence model.
(d) All phases show the same pressure (no surface tension, no solid compression).

In the multi-fluid model, there is one solution field separately for each phase. The phases have different velocity and temperature distributions, but have the tendency to equalize through either empirical interface drag forces and heat transfer terms. Furthermore inter-phase non-drag forces are considered (virtual mass force, lift force, wall lubrication force, turbulent dispersion force, solids pressure force). The solids pressure force describes the interaction of particles as they approach their packing limit; when the volume fraction comes within 0.001 of the maximum packing fraction (set at 0.62), an extra friction velocity is added to the shear velocity.

The interface drag forces are empirical correlations. Two mechanisms are considered exerting a drag on an immersed particle by a moving fluid: (i) skin friction due to the viscous surface shear stress, and (ii) form drag due to the pressure distribution around the particle. The total drag force is expressed in terms of a dimensionless drag coefficient which is, for particles of a given shape moving in an incompressible Newtonian fluid, a function of the Reynolds number only. Standard solid particle drag curve for spherical shape (if surface tension can be neglected) is applied. For compressible fluids, the correlations for incompressible flows are valid up to Ma = 0.3. For higher Mach numbers, the drag coefficient will be a function of Re and Ma.
Heat transfer processes across phase boundaries are not an issue in this study, since the heat production in the moderator was not considered.

The turbulent multi-phase model is a simple generalization of the single-phase turbulence modeling. The individual phases are allowed to be declared turbulent or laminar. The additional production and dissipation of turbulence at the presence of more than one phase, which is not covered by single-phase source terms could be taken into account by implementing own respective models (which was not done for this study). Large particles, for instance, create turbulence due to the turbulent wake behind the particles; on the other hand, small particles tend to suppress turbulence.

2.2. Moderator Chamber Design

The design for the moderator chamber selected for this study was based on the latest concept for the ESS cryogenic moderator chamber (for LH$_2$) as has been suggested by Soukhanov [3], which is characterized by a horizontally arranged inlet/outlet fluid flow. It was modified such that the fluid entering the chamber through the central inlet flow tube will hit onto semi-spherically shaped walls to allow for a smooth return flow and avoid as much as possible a deposition of particles in dead zones. A splitting edge between the semi-spheres is to subdivide the flow into two parts with the fluid flowing through the upper and lower half of the chamber on its return and exiting the chamber in an annular flow around the inlet tube.

![Figure 1. Calculation grids for first part (top) and second part (bottom) of the study](image)

A two-dimensional, body-fitted calculation grid for the moderator chamber has been established as is shown in Fig. 1. The dimensions are 310 mm as maximum length and 160 mm in height. The extension in the third dimension, which is formally present, is one mesh row with the arbitrary thickness of 20 mm. The whole calculation grid as used in the beginning of the study (see Fig. 1, top) consists of a total of 7244 mesh volume elements.

The inlet flow is centrally from the right side, the outlet is above and below the inlet to the right side. Inlet and outlet flows are separated by 2 mm thin walls (no-flow regions), which are extended to the central points of the semi-spheres on the left side. The two semi-spheres are connected by the above mentioned splitting edge with a thickness of 2 mm in-
truding horizontally approximately 20 mm into the chamber. The outer walls have a thickness of 3 mm and are considered “conducting walls” meaning that heat transport by conduction is being taken into account.

The wall material is the aluminum alloy AlMg3, i.e., the respective correlation for the temperature dependent thermal conductivity was assumed [4].

For a second part of this study, two major changes of the calculation grid were made (see Fig. 1, bottom). Due to the experience of long duration for the computer runs, a somewhat more coarse grid was created reducing the number of elements by more than half down to 3020. Furthermore the splitting edge was prolonged until back to the entrance of the chamber. The purpose of this separating wall was to force half of the entering – at this point still homogeneously distributed – two-phase fluid to take the route through the upper part of the chamber. By this means, the flows through both parts of the chamber were physically decoupled and the moderator split into two independent flow systems.

2.3. Initial and Boundary Conditions

The two-phase fluid to be investigated here consists of liquid hydrogen as the continuous phase and solid methane hydrate pellets (and in one case methane pellets) as the disperse phase. All pellets are assumed to be of the same size and a spherical shape with 0.5 mm diameter throughout the domain. The reason for the assumption of such a small diameter is to increase the chance for the particles to be borne by the continuous phase. The difference in the densities of methane hydrate and LH2 result in a very high density ratio, which is close to that for the system of LH2 plus water ice of 14:1. The densities assumed were 70.8 kg/m³ for LH2 and 920 kg/m³ for methane hydrate. The fraction of the disperse phase in the inlet flow was initially set at 20 vol% and later consecutively increased to 30 vol% and 40 vol%, respectively. These volume fractions correspond to mass fractions of 76 %, 85 %, and 90 %, respectively.

The inlet temperature of the two-phase flow was set at 25 K. Since for this study, no heat sources were taken into account and also adiabatic boundary conditions were assumed, the outlet temperature is also 25 K.

The assumption for the velocity of both phases at the inlet was set at 4 m/s, which translates into a mass flow of 0.763 kg/s for the selected calculation grid. It is based on the fact that in previous studies on this moderator design employing pure LH2 as fluid and assuming a heat source as anticipated for the ESS cryogenic moderator (7.5 kW in the real-size moderator chamber), the increase of the fluid temperature between inlet and outlet (average) was limited to about 3 K.

2.4. Numerical Behavior

The computer simulation for a case to be considered was conducted as a transient calculation in consecutive steps. The first run was started with a 20 vol% fraction of the solid phase in the inlet flow. After reaching approximately an equilibrium state, the solid phase fraction was raised and the calculation continued until again a more or less equilibrium state was obtained. The calculation for a specific solid phase fraction was interrupted once in a while to check things like convergence behavior, and eventually restarted, often with modified numerical parameters and/or time step width, if an improvement was expected. Time steps were typically varied in the range of $10^{-2}$ to $10^{-4}$ s, where the fluid proceeds in the order of mm. The results for cases with a lower particle volume fraction are the starting point for the cases with a higher particle volume fraction. The calculation was usually stopped after the fluid has traveled a distance corresponding to several times the distance of once through the moderator chamber. CPU times became significantly smaller for the calculations based on the second, simplified grid.
3. TWO-PHASE FLOW PATTERN IN THE MODERATOR CHAMBER

3.1. Results with the first calculation grid

For the first part of the study, the moderator design as shown in Fig. 1, top, was considered. Starting with a two-phase flow consisting of 20 vol% of methane hydrate particles, the calculational results for the distribution of the volume fraction of the LH₂ and the methane hydrate particles, respectively, in the moderator chamber are shown in Fig. 2. The figures indicate the complementary character of the two distributions with the volume fraction for the methane hydrate volume fraction ranging between 0 and about 64 % (Fig. 2, top) and the LH₂ ranging between approximately 36 % and 100 % (Fig. 2, bottom).

![Figure 2](image-url)

The particle phase of the inlet flow shows soon the tendency to sink and preferably pass through the lower half of the moderator, whereas only a smaller part of the particles contributes to the outflow through the upper half of the moderator. The red colored areas represent-
ing high volume fractions indicate zones of enhanced concentration of particles (Fig. 2, bottom) or zones of almost pure LH\textsubscript{2} (Fig. 2, top), respectively. The transition from high to low concentration areas is relatively sharp.

Figure 3. Methane hydrate pellets (top) and LH\textsubscript{2} (bottom) velocity distribution for 20 vol\% of pellets in the inlet flow for the first calculation grid

The methane hydrate pellets are mainly concentrated at the turning points of the flow in both chamber halves and, to a particularly large extent, at the bottom of the lower half of the chamber. In these zones, the pellet concentration has almost reached its maximum. From the calculated velocity distribution, it can be concluded that the low values for the particles in those zones indicate a strong tendency towards a slow-down of the flow or even deposition with velocities having dropped from 4 m/s at the entrance to around 1 m/s and less. But also the velocity of the LH\textsubscript{2} is here significantly smaller and in the same order of magnitude as for the particles.

The area immediately below the separation wall in the upper moderator half is a location with prevailing continuous phase at low velocities. High-velocity regions are found at the turning points where, due to the large particle concentration adjacent to the spherically shaped walls, only a narrow gap at the end of the separating walls remains open for the faster flowing LH\textsubscript{2} or particles.

Immediately after passing the turning points on its way back to the exit, the two-phase flow has developed recirculation zones, a larger one in the upper half of the chamber with the
continuous phase dominating, and a smaller one in the lower half, where a large part is occupied by a high concentration of particles.

The velocity distribution of the two phases is shown in Fig. 3 indicated both by color and by length of the arrows. It is found to be slightly different for the upper and lower part of the moderator due to the different quantities of particles passing through this part. Starting with a value of 4 m/s at the inlet as initial condition, zones of enhanced velocities are found close to the turning points and at the outlet, reaching in the upper part values of around 6 m/s (particles) and 8 m/s (LH$_2$), and in the lower part 4 m/s (particles) and 5 m/s (LH$_2$), respectively. Slow-flow regions are principally found where particles have accumulated.

30 % volume fraction of methane hydrate pellets in the inlet flow

The comparison with the follow-on calculation after raising the fraction of the particle phase at the inlet from 20 to 30 vol% (≈ 85 mass%) shows that the regions with high particle concentration have slightly further expanded, now more and more affecting the space in the inlet tube, particularly in the lower part.

The velocity distribution has qualitatively hardly changed. The maximum figures at both the turning point and the exit are approximately the same for both the particles and the liquid.

The wavy shape of the surface of the particle bed in the bottom half of the chamber appears to be a sign of ongoing re-distribution by deposition and remobilization processes.

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The wavy shape of the surface of the particle bed in the bottom half of the chamber appears to be a sign of ongoing re-distribution by deposition and remobilization processes.

40 % volume fraction of methane hydrate pellets in the inlet flow

The attempt to calculate the case with a further increased particle fraction at the inlet to 40 vol% was unsuccessful. It was presumably due to a plugging of the flow paths inside the moderator chamber, which the computer model was obviously not able to handle. Rather than trying to overcome the difficulties by playing with the numerical parameters, a restart of the calculation was made on the basis of a modified calculation grid.

3.2. Results with the Second Calculation Grid

For the second part of the study, two major changes of the calculation domain were made:
1. The number of volume elements was cut to less than half in order to significantly reduce the computation time for a run.

2. The short piece of wall connecting the two semi-spherical walls at the end of the moderator chamber was extended through the whole inlet tube, in order to force exactly half of the particles and the liquid hydrogen to go through the upper and lower part of the moderator chamber.

The consequence of the second item was a complete disconnection of the two halves of the moderator leading to two independent calculations. The modified calculation grid is shown in the bottom part of Fig. 1.

20 % volume fraction of methane hydrate pellets in the inlet flow

The calculation was started again with a 20 vol% fraction of particles at the inlet. Since the inlet velocity remained fixed at 4 m/s, the absolute mass flow was slightly reduced (LH₂: 0.181 → 0.172 kg/s; methane hydrate pellets: 0.582 → 0.553 kg/s) due to the fact that the inlet cross section became somewhat smaller by the wall, which separates the chamber into halves.

![Figure 5](image)

**Figure 5.** Methane hydrate pellets concentration and velocity distribution for 20 vol% of pellets in the inlet flow for the second calculation grid

Fig. 5 shows the pellet concentration distribution together with the respective velocity distribution. Now that half of the pellets (and of the LH₂) were forced to pass through either chamber half, the regions of high particle concentration have drastically changed their pattern. Compared to the corresponding calculation with the previous grid (see Fig. 2, top), the area with maximum particle concentration in the lower half is still found at the bottom on their way out of the chamber, but its size is much smaller because of the lower quantity of particles passing through this part. Also on top of the wall separating inlet and outlet flow, a narrow strip of high particle concentration can be identified, which is larger than in the previous case.

For the upper half of the moderator, now experiencing a much higher particle flow, highest particle densities are observed near the outer wall surfaces, in particular in the semisphere around the turning point, where it appears to be difficult for the LH₂ to carry the heavier particles away against the gravitation force and rather accumulate inside the semispherical shell.
Also the velocity pattern has changed compared to the respective case with the first calculation grid. Due to the fact of a larger number of particles passing through the upper moderator half, the velocity of the pellets has somewhat decreased in the open gap near the turning point (to approx. 4 m/s). The velocity profile at the chamber exit has become more or less symmetrical, whereas in case of the first grid, there are higher velocities for both phases at the upper exit due to the lower particle density.

**30 % volume fraction of methane hydrate pellets in the inlet flow**

The plugging effect in the upper chamber half is further intensified when the particle fraction is raised to 30 vol%. As can be seen from Fig. 6, a thicker layer with maximum particle density (of around 63 %) is found just below the outer wall, where all outflowing particles seem to be concentrated. In the inlet tube, an increasing region of high particle density at the bottom can be recognized. The large mass of particles in the semi-sphere reacts as a barrier for the continuously incoming particles, shifting the boundary between high and low particle concentration further towards the inlet.

![Figure 6](image_url)  
**Figure 6.** Methane hydrate concentration and velocity distribution for 30 vol% of pellets in the inlet flow for the second calculation grid

In the lower moderator half, there is also a significant growth of the high particle density layer both upon the wall separating inlet and outlet flow, and at the bottom in the outlet flow region. The liquid phase dominating in the upper part of the inlet flow does not allow a too strong accumulation in the semi-sphere region and rather carries the particles into the bottom part where the accumulating particles gradually start plugging the exit flow.

Velocities have somewhat increased in the regions with low particle density near the turning points and the exit reaching around 6 m/s (pellets) and 8 m/s (LH₂), respectively.

**40 % volume fraction of methane hydrate pellets in the inlet flow**

The further raising of the methane hydrate pellets volume fraction to 40 % leads to an intensive concentration of the pellets in the lower part of the upper moderator half, filling it up until fairly close to the inlet. Near the turning point, the maximum pellet concentration has reached already the wall separating inlet and outlet flow. The outlet flow region in the upper part of the upper chamber half remains almost unchanged with a pellet layer near the outer wall and a sharp transition to the almost pellet-free area below. A slight thickening of the pellet layer can be identified near the exit where the tube becomes more narrow.
Also in the lower half of the moderator, the areas with high pellet densities have further increased both above and below the separating wall leaving only a small space for the faster traveling LH₂ and pellet flows in the low particle density region and, thus, leading to a strong velocity gradient at the exit.

A comparison of the two halves of the moderator chamber shows the difference in the flow pattern. The larger resistance of the pellets of being transported upwards at the turning point, as is the case in the upper half, results in a significant accumulation of particles in the inlet region. In the lower chamber half, where particles are being transported downwards at the turning point, it is the exit region that accumulates particles in most of its area to the maximum density.

**Figure 7.** Methane hydrate pellets concentration and velocity distribution for 40 vol% of pellets in the inlet flow for the second calculation grid

**Solid methane pellets as disperse phase**

Finally some calculations were conducted to investigate the behavior of the equally sized, but lighter methane pellets compared to the methane hydrate pellets. The density ratio of disperse over continuous phase is, thus, reduced (from 13) to about 6. Again the second calculation grid was taken to examine in particular whether the (now) lighter particles are easier carried away with the LH₂ flow. Unlike the previous calculations, this case was started with an inlet flow with a 30 vol% fraction of methane pellets. The results are shown in Fig. 8, which is to be compared with the respective case for methane hydrate pellets given in Fig. 6.

For the upper chamber half, a difference can be identified in the inlet flow section, where the deposition behavior particularly before reaching the turning point, is much less extended than is the case with the heavier methane hydrate pellets. Still, most part of the hemisphere has reached maximum particle density. The flow pattern on the return path practically remained unchanged with the high particle density region being attached in a narrow layer below the outer wall surface.

There is even a larger difference in the flow pattern for the lower chamber half. The lower weight of the pellets reduces their tendency to sink within the inlet section reducing the number of particles, which accumulate on the separating wall. Inside the hemisphere and all along the way to the exit, there is only a small layer on the wall surface, which has maximum particle density, indicating that most particles will leave the chamber without accumulating inside.
This picture, however, changes when the solid phase fraction at the inlet is increased to 40 vol% (see Fig. 9). The tendency to block the exit is seen again both in the inlet part of the lower chamber half before reaching the exit.

Furthermore this calculation has revealed a relatively strong variation of the exit mass flow for both L.H₂ and particles, meaning that hardly any equilibrium state has been reached during the transient calculation and presumably will not be reached. It appears that occasionally, obviously when the plugging effect is dominant, all of a sudden a larger portion of particles is being carried out of the chamber, before the regions freed of particles start to be refilled again. First indications of such a behavior were already given with the observation of the “wavy shape” of the high particle density regions interpreted as a relocation of the solid phase.
4. CONCLUSIONS

The objective of this study was to examine the flow behavior of a solid-liquid (methane hydrate/methane-liquid hydrogen) fluid through a given design of a moderator chamber for the ESS target system. The calculations under simplified conditions, e.g., taking no account of heat input from outside, have shown first that the computer code used, CFX, was able to simulate the behavior of a dispersed two-phase flow through the moderator chamber, producing reasonable results up to a certain level of the solid phase fraction, that allowed a continuous flow process through the chamber. Inlet flows with solid phase fractions beyond 40 vol% were found to be a “problem” for the computer code. This may be interpreted as either a “numerical problem” or a “real flow problem” or a combination of both.

From the computer simulations based on solid phase fractions between 20 and 40 vol% in the inlet flow, it was observed that with increasing solid phase fraction at the inlet, the resulting flow pattern reveals a strong tendency for blockage within the chamber, supported by the “heavy weight” of the pellets compared to the carrying liquid. Locations which are prone to the development of such uneven flow behavior are the areas around the turning points in the semispheres and near the exits of both moderator halves.

From the neutronic point of view, a high particle density in the moderator chamber is desirable. It is, however, in question whether under such circumstances, the flow conditions of the two-phase fluid system can be maintained such that no blockage of the flow occurs with the risk of a too long residence time of the pellets in the moderator chamber. For the investigated solid phase fractions between 20 and 40 vol%, there appeared to exist also a transient behavior of the flow pattern with a continuous variation of the inlet/outlet balance of both phases, indicating relocation processes of the pellets in high particle density regions.

The considered moderator chamber with horizontal inlet and outlet flow for a solid-liquid two-phase fluid does not seem to be an appropriate design. Modifications in the design should focus on the avoidance of pellet movement against gravitation and rather concentrate on a top-down vertical movement through the moderator.

REFERENCES

ABSTRACT

We survey the results of an earlier study of the inelastic scattering from solid ammonia, and report the results of a preliminary experiment carried out at the ~100 μeV-resolution quasielastic scattering spectrometer QENS at IPNS.

1. INTRODUCTION

Solid ammonia is an attractive candidate for a cold moderator material because of its high proton density. Absorption losses due to $^{14}$N can be avoided by using ammonia enriched in the isotope $^{15}$N. Solid $^{15}$NH$_3$ could be used in a pelletized moderator as an alternative to pellets of methane. Other advantages and disadvantages of ammonia as a moderator have been previously discussed [1]. However, we do not know enough about ammonia’s low temperature thermalization properties (i.e., density of states at meV energies). The present experiment was intended to look for low-energy modes in solid ammonia that could be used in ultra-cold moderators, and to provide information on which to base the construction of scattering kernels.

2. PREVIOUS MEASUREMENTS

Ammonia has a melting point of about 195.45 K and a boiling point of about 239.8 K. Its solid density is 0.83 g/cm$^3$ for temperatures just below its melting point and about 0.86 g/cm$^3$ at 77 K [1,2]. Despite its high proton density ($0.88 \times 10^{23}$/cm$^3$ vs. $0.78 \times 10^{23}$/cm$^3$ for solid methane), and thus its potential for use as a cold moderator, there appear to be no high-resolution measurements of neutron scattering from solid ammonia.

One set of somewhat lower-resolution neutron inelastic-scatter measurements was made by Goyal et al. [3] for solid ammonia at 106 K. Calculations of the Debye temperatures using their frequency distribution function $g(\omega)$ (shown in Figure 2) compared favorably with those obtained from measured specific heat data.

There are in addition a number of measurements of excitation frequencies in the infrared region [4,5]. These show the absorption lines listed in Table 9 below. Since these lines were measured in the gas phase, they represent internal molecular vibrations of the ammonia molecule. Although they are at higher energies than required for use as a cold moderator, these lines might be seen in neutron inelastic scattering measurements where the range of energy transfer measured is sufficiently large. Moreover, these are essential components of the scattering function.
Table 9. Tabulated infrared absorption wavelengths [4-6].

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</table>

3. EXPERIMENTS

We conducted an experiment to measure neutron inelastic scattering from solid and liquid ammonia using the QENS [7] instrument at the Intense Pulsed Neutron Source at Argonne National Laboratory in March 2002. QENS is a spallation-source-based “crystal-analyzer” or “inverse-geometry” spectrometer. The instrument accepts a white neutron beam from a solid methane moderator onto the sample. The average energy resolution of the spectrometer is 90 µeV. Inelastic scattering was recorded on 145 He³ detectors oriented from 2θ = 20° to 145° (average scattering angle is 2θ = 90°) resulting in a Q range extending from 0.3 up to 2.6 Å⁻¹. In QENS, sample diffraction is measured at the same time as inelastic scattering on two diffraction banks of 7 He³ detectors each, oriented at average scattering angles of 2θ = 10° and 2θ = 155°, resulting in a global diffraction Q range extending from 0.05 to 35 Å⁻¹.

The aluminum sample container was a cylindrical annular volume 50 microns thick, approximately 1.25 cm outer diameter, and 10 cm high. Based on this sample geometry and the NH₃ neutron scattering cross-section, we estimated the sample transmission to be 0.85. The sample container was filled by first evacuating the sample cell at room temperature, cooling the cell down to about 210 K (at which temperature NH₃ is a liquid), and then opening a valve at the entrance to the sample cell to connect the sample cell with a standard volume that had been charged with NH₃ to about 2 atm. By cooling the sample cell from the bottom and condensing the gas into the liquid phase (see Figure 3), we avoided causing a blockage due to frozen NH₃ in the fill line. The sample mass calculated as the product of the
sample volume and the nominal density of solid NH$_3$ was about 167 mg. Using the drop in the filling system pressure and the volume of the filling system, the sample mass was calculated at about 128 mg. These two estimates are in agreement to within 25% or so. Our knowledge of the sample volume and the material density were not precise.

After the pressure in the filling system had stabilized, we closed off the sample cell and cooled the sample down to a control temperature of 30 K. Measurements were taken for 12-hour runs at nominal temperatures of 30, 50, 90, 140, and 210 K (the last of these is liquid), with the temperature measured at the cold head of the displex. Temperature measured at the top of the sample container was about 10 K higher. The runs also included an empty cell measurement and a vanadium rod for normalization.

![Figure 3. (above) Sample container fill system. (below) Sample container attached to displex cooler.](image)

During the experiment, the quantity measured is the number of neutrons scattered per unit solid angle $d\Omega$ and per unit energy $d\omega$:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_i}{k_f} S(Q, \omega)$$
We also define:

\[ \bar{Q} = \vec{k}_i - \vec{k}_f \]
\[ \hbar \omega = E_i - E_f \]

where \( \vec{k}_i \), \( \vec{k}_f \) and \( E_i, E_f \) are the neutron wave vectors and energies before (i) and after (f) the scattering process. \( Q \) and \( \omega \) are the neutron momentum and energy transfer. \( S(Q, \omega) \) is the dynamical structure factor.

If we consider only the inelastic region of the spectrum, and if all multi-phonon processes are neglected, \( S(Q, \omega) \) may be written in the form:

\[
S(Q, \omega) = \frac{\sigma_{inc}}{4\pi} \exp(-2W(Q)) \left[ \delta(\omega) + \frac{\hbar Q^2 g(\omega)}{2m\omega} n_B(\omega) \delta(E - \hbar \omega) \right]
\]

where \( n_p(\omega) = \left[ 1 - \exp(-\hbar \omega/k_B T) \right]^{-1} \) is the Bose population factor, \( m \) the neutron mass, \( W(Q) = \frac{1}{2}(Q^2 a^2) \) is the Debye-Waller factor, \( g(\omega) \) is the generalized vibrational density of states. \( E \) is the energy of a transition in the system.

After scattering from the empty sample container was subtracted, the raw data were normalized to the monitor detectors and to scattering from a vanadium rod. No absorption corrections were applied and multiple scattering was neglected. Inelastic detectors having elastic \( Q \) corresponding to Bragg peaks observed on the diffraction detectors were removed from data treatment. The data from all remaining angles were summed together, and then corrected by Bose occupation and \( k_f/k_i \) factors.

In order to deal with absolute scattering intensities, the data have been normalized to \( K \), the extrapolated scattered elastic intensity at \( Q=0 \) (see Figure 4). The constant \( K \) accounts for the total scattering cross section of \( \text{NH}_3 \) in the beam (product of the sample mass and cross section) and includes the angular range of integration. Figure 4 shows that the elastic scattering is nearly constant with \( Q \) for the solid material, and has a value at \( Q = 0 \) of about \( \exp(7.236) = 1390 \).

![Figure 4. Integral over the elastic scattering peak.](image-url)
The results presented in this paper are the NH₃ density of states $g(\omega)$:

$$g(\omega) = \frac{1}{K*\sigma_{\omega}(\omega)} \int_{n_{\omega}} \int_{k_{f}} \left( \frac{d^2\sigma}{d\Omega d\omega} \right) d^2\theta$$

where $\left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{\omega}$ is the experimental scattered intensity normalized to the monitor detector and to vanadium.

4. ANALYSIS AND DISCUSSION

Figure 5 shows the density of states function $g(\omega)$ over the energy transfer range 0.5-10 meV. From these data, it does not appear that there are any low-energy modes available in NH₃ that would support neutron thermalization down to meV energies. There is a faint hint of a level at around 6 meV in the data for 30 K, but a full statistical treatment of the data needs to be performed before determining whether or not this is real.

Figure 6 shows the density of states function over the energy transfer range 0-80 meV. In this figure, the analyzed data were combined into energy bins on a logarithmic scale having 20 bins per decade in energy. The feature in Goyal’s measurement (Figure 2) that shows up as a single mode at about 13 meV appears in our measurements to be two individual lines spaced closely together at about 9 and 11 meV. These lines are not individually visible at the resolution used by Goyal et al. We see also a mode at about 19 meV, with a suggestion of another mode at 23 meV in the higher-energy shoulder of the 19-meV mode. Figure 7 shows the same data up to 250 meV. In the range 100-250 meV, our logarithmic energy binning obscures some of the details of the $g(\omega)$ function that are seen when averaging over smaller
intervals. Thus some excitation energies that are shown in Table 10 below are not seen in Figure 6.

**Figure 6.** Angle-integrated $S(Q,\omega)$ over the energy transfer range 0-80 meV. Successive curves are displaced vertically upwards by 0.05.

**Figure 7.** Angle-integrated $S(Q,\omega)$ over the energy transfer range 0-250 meV.

Table 10 summarizes the energy transfer spectral data from the references cited earlier, as well as modes that could possible be identified from the present set of measurements. Our data at higher Q (above about 250 meV) do not have good enough statistics to warrant identification of individual lines.
Table 10. Summary of energy transfer spectrum data.

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5. REFERENCES

ABSTRACT

To estimate the neutronic characteristics of methane hydrate and also to synthesize cross section data for simulation we need neutron scattering data ranging wide energy and momentum region. We performed inelastic neutron scattering experiments to get information about the neutron cross section on methane hydrate. It was found that at high momentum transfer region rotational mode as well as vibration mode showed recoil like behavior. On the other hand, at low momentum region, as well known, free rotation like energy levels were observed. The energy level of ice in methane hydrate was very similar to normal ice. The results suggest that the rough expression of the cross section of the methane hydrate is presented by linear combination of the methane and ice.

1. INTRODUCTION

It has been proved that methane is the best material for the cold moderator[1]. On the other hand ice at 20K gives higher neutron intensity around the thermal neutron region[1]. Methane hydrate consists of these tow materials. So, it is expected that the methane hydrate moderator give the higher intensity for a wide energy region ranging from cold to thermal neutron energy. Therefore, the methane hydrate has been proposed as a new cold moderator material.

To evaluate the neutronic characteristics of methane hydrate it is necessary to perform moderator experiments as well as to obtain the cross section data for understanding the characteristics and also to perform the simulation since in the experiments we get information under the restrict conditions. However, there exist very small number of cross section data and they aimed at knowing the dynamics of methane in the hydrate. Furthermore, the energy range studied was concentrated at low energy[2-4]. To know the moderator neutronics we should know the neutron scattering cross section in the wide energy and momentum region and also the total neutron cross section.

For this purpose we performed neutron inelastic scattering experiments. Here, we briefly mention about the preliminary consideration on the results of the scattering experiment.
2. EXPERIMENTAL

Methane hydrate was prepared by contacting methane gas with crashed ice in a high pressure container under a condition of pressure of 5 MPa and temperature of 268K. The methane contents in the hydrate were at least 80% and contents of many of samples were around 90%. We prepared CH$_4$-H$_2$O and CH$_4$-D$_2$O, and also prepared H$_2$O and D$_2$O ice for comparison.

Neutron scattering experiments were performed on the MARI spectrometer at ISIS, and on the LAM-80 at KENS. The energy resolution of LAM-80 is about 0.02 meV. The sample temperature was mainly about 12K. Higher temperatures were also examined on MARI to study the effect of the temperature on the rotational level, although the results are not described here.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

We got wide energy and momentum range scattering data by using MARI. Scattering intensity map obtained by incident energy of 500 meV are shown in Fig. 1 for CH$_4$-D$_2$O and CH$_4$-H$_2$O. The left figure is for CH$_4$-D$_2$O and the right figure for CH$_4$-H$_2$O. From the left figure we recognize recoil like behavior at high Q region not only at low but also at high energy regions. The lowest curve would correspond to rotation, middle one consist of two libration levels of 163 and 190 meV and the highest 362 and 374 meV. This situation is different from the pattern of the right one, which shows the contribution from ice indicating the energy levels independent of Q. They belong to lattice or vibration modes of ice.

Where the recoil like behavior comes from? We assumed that the rotation mode would be

\[ E = E_0 + E_Q, \quad E_Q = \frac{\hbar^2 Q^2}{2M}. \]

represented by energy conservation formula of the recoil,

Here, $E_0$ is the energy level and $E_Q$ is the recoil energy. We applied this formula to the lowest line indicated by (1) and obtained the effective mass of 2.64 m, which is very close to the effective mass of the free rotation, 2.67 m, where m is the hydrogen mass. Recoil like behavior of the libration modes assumed to be coupling with the rotational mode. We applied
the formula also to the libration modes of around 170 (2) and 370 meV (3), and get the effective masses of 2.71 m and 3.13 m, respectively. They are also close to the free rotation effective mass. So, the recoil may be due to rotation.

To get the information about the lattice mode in detail we obtained data with an incident energy of 100 meV. Scattering intensity against the neutron energy is shown in Fig. 2, where we compared the intensities between methane hydrate and ice. We can see several peaks in both intensity spectra and there is almost no difference between them. The levels observed are assigned to TA mode of 8.8 meV, LA mode of 18 meV, TO mode of 27 meV and TO mode of 35 meV. Librational modes appeared above about 65 meV. This suggests that around this energy region the neutron cross section of methane hydrate is expressed by linear combination of each material, methane and ice.

To investigate the low energy level we performed experiments using an incident energy of 15 meV. Scattering intensity maps are indicated in Fig. 3 for CH$_4$-D$_2$O and D$_2$O. It is clearly recognized the energy levels originated from methane hydrate by comparing the spectra. The level below 5 meV would be attributed to the methane mode. Level assignment is shown in Fig.4.

![Figure 2. Lattice modes of H$_2$O in methane hydrate and ice](image1)

![Figure 3. Scattering intensities from CH$_4$-D$_2$O and D$_2$O](image2)
The tentative assignments are as follows. The levels labeled a, b, c and d would be rotational levels of transitions, J=0 to 1,2,3 and 4, respectively. A and B would correspond J=1 to 2 and 3. Here, J is the quantum number of the rotation level. The rotational energy levels observed are almost the same as those of the free rotation and would be vibration of the methane molecule in the large and the small cages.

Finally we tried to measure a tunneling level of the rotational mode since there may be little difference between observed and free rotation. The energy level of the methane rotation will be split by potential around the methane molecule. The measurements was performed on LAM-80 at KENS. Fig. 5 shows the scattering data, which shows weak peak around 0.5 meV and quasi-elastic like tail around the elastic peak. Rise of intensity starting from 0.8 meV is due to the first rotational level around 1 meV. We found that the peak around 0.5 meV is spurious one due to the mica analyzer. So, there is no peak due to the splitting of the rotational levels.

\[ S_{mc}^{R}(Q, \omega) = j_0^2(\tilde{Q} d) \delta(\omega) + \sum_{l=1}^{\infty} (2l + 1) j_l^2(\tilde{Q} d) F_l(\omega) \]

\[ F_l(\omega) = \frac{1}{\pi} \frac{1(l + 1)D_l}{\omega^2 + [1(l + 1)D_l]^2}. \]
By fitting this function to the experimental results we get rotational diffusion constant $D_r = 0.44 /\text{psec}$. However, we need more careful experiment to confirm the tail is real or not.

4. CONCLUSIONS

We performed the inelastic neutron scattering to investigate the cross section of methane hydrate. The results suggest that the dynamic mode of the methane and ice are almost independent although there exist the new modes of vibrations of methane in cages. We are now proceeding the synthesis the cross section model for methane hydrate. We need further data depending temperature and the total neutron cross section.

ACKNOWLEDGEMENTS

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REFERENCES

Structural phase transitions and dynamics of solid mesitylene investigated by
diffraction and inelastic incoherent neutron scattering methods

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ABSTRACT

The results of simultaneous investigations of neutron powder diffraction (NPD) and
inelastic incoherent neutron scattering (IINS) performed at the IBR-2 pulsed reactor of the
JINR in Dubna are presented. It is shown that solid mesitylene can exist in different crystallo-
graphic structures depending on the cooling rate and thermal procedure. The phase I, which
can be obtained by annealing of solid mesitylene at (200–220)K, is stable from the melting
point at 227K down to liquid He temperatures. The phase II, obtained when freezing over-
cooled liquid, can pass to the phase III at about 90K. Generalized density of phonon states of
these three crystallographic phases have been obtained from their IINS spectra at 20K. The
frequencies of methyl librations in phase III are determined at 19.2 and 23.3 meV. These
modes in phases I and II are shifted down to the lattice mode frequencies below 15 meV.

1. INTRODUCTION

Mesitylene, or 1,3,5-trimethylbenzene, \( C_6H_3(CH_3)_3 \), is a well known organic solvent
characterized by the relatively low freezing (227K) and high boiling (437K) temperatures.
Because of the high content of hydrogen and the assumed weakly hindered rotation of methyl
groups in the solid phase, which can remove energy from neutrons, this compound has been
recommended as a neutron moderator [1], and used for the construction of the TCNS cold
neutron source at the TRIGA Mark II pulsed reactor of the NETL in Austin [2]. However, the
structure and dynamics of solid mesitylene has not been well investigated until recently.

The temperature dependence of the IINS spectra has confirmed the occurrence of the
rotational freedom of the methyl groups in solid mesitylene at \( T=100K \), but at \( T=20K \) the
rotational jumps seem to be frozen out [3]. The NDP spectra, measured in this experiment for
lattice spacings up to 0.6 nm, did not indicate any diffraction peaks.

The Raman spectra of \( C_6H_3(CH_3)_3 \) indicate some changes in the temperature depend-
ence of the lattice modes and certain internal modes at 95K and 195K [4]. The DSC thermo-
graphs reported in [4] show two endothermic peaks for solid mesitylene: a strong one at 91K
and a very weak one at 188K, respectively. The following three endothermic peaks at 220K,
222K and 227K, correspond to the melting of the samples at different heating rates. This re-
sult was interpreted as the manifestation of three different structural modifications: \( I_\alpha \), \( I_\beta \) and
\( I_\gamma \) of the high-temperature solid phase.

Our recent results of the NPD and IINS investigations of mesitylene-D3, \( C_6D_3(CH_3)_3 \),
and mesitylene-D12, \( C_6D_3(CD_3)_3 \), show up that solid mesitylene can exist in various crystal-
lographic structures, depending on the cooling rate. At a cooling rate of 2K/min, the
undercooled liquid was freezing in the structure of phase II, and the first order structural
phase transitions from phase II to phase III were detected at ~90 K for mesitylene-D3, and at
~100K for mesitylene-D12. Transition from phase II to phase I is not reversible, it starts at
approx. 190K, but a diffraction pattern of pure phase I was observed only after annealing of
the samples at 220K. This high temperature phase has only one structural modification and at
cooling becomes stable with respect to phases II and III. Phase II, when cooled from 200K in
the presence of phase I nucleations, can be also undercooled to liquid He temperatures [5].

Thus, three different solid phases of mesitylene can exist and investigated at low tem-
peratures. Here we present in more detail the results of NPD and IINS investigations of me-
sitylene-D3 and -D0, which were performed in order to check whether these phases detected
for deuterated samples can be obtained and observed in the protonated substance as well.

2. EXPERIMENTAL

Commercial mesitylene 99%, 1,3,5-(CH₃)₃C₆H₃, was purchased from the Aldrich Com-
pany. The deuterated samples of mesitylene-D3 and –D9 were purchased from the Russian
Scientific Center „Prikладная Chimia” at St. Petersburg. For these samples the isotopic pu-
rity of the deuterated groups was guaranteed to be better than 98%.

Rectangular sample holders of dimensions 15x7 cm² and a volume of 9 cm³ made from
Al-plates of 1mm thick, were used for the neutron scattering experiments. The sample holders
were placed in the top loaded shaft-type cryostat cooled by the LEYBOLD-HERAEUS R-
l040 type closed cycle helium refrigerator. A typical cooling rate of 2 K/min is achieved
when cryostat and sample are cooled down from room temperature to 20 K. When a sample
within the standard holder at room temperature has been fixed to the cryostat shaft and cooled
to 20K, the average cooling rate was 5 K/min. The cooling rate of 100K/min, from 290K
down to 77K, was achieved by rapid cooling of the sample in a liquid nitrogen bath.

The NPD and IINS spectra were measured simultaneously at the inverted geometry
time-of-flight spectrometer NERA at the high flux pulsed reactor IBR-2 of the Joint Institute
for Nuclear Research in Dubna. The NERA spectrometer allows recording the IINS and NPD
spectra from 0.5 Å up to 7 Å of incident neutron wavelength. The 16 IINS spectra are re-
corded at scattering angles from 20° up to 160°, with interval of 10°. Simultaneously, several
detectors can record the NPD spectra at two sectors of the scattering angles: 120° – 150° and
30° – 60°, which practically allows one to measure lattice spacing in the range 0.1 – 1 nm. The
incident neutron wavelength of the NPD spectra is determined by measuring the neutron time-
of-flight from the IBR-2 moderator to the NPD detector in a distance of 110.45 m. This al-
loWS determining the lattice spacing in the range of 0.2 - 0.5 nm within a resolution of 0.2 -
0.5 %, using the real neutron pulse width (0.2-0.3 ms) of the IBR-2.

In the case of inelastic scattering, the energy of scattered neutrons is selected by cooled
beryllium filters and pyrolytic graphite neutron wave-length analyzers, placed before the de-
tectors. The elastic line of the NERA spectrometer is fixed at a neutron wave-length of
4.25 Å, which corresponds to 4.53 meV of the final energy of scattered neutrons. The FWHM
of elastic line is 0.6 meV. The incident neutron energies for the IINS are determined by
measuring the neutron time-of-flight from the IBR-2 moderator to the sample in a distance of
109.05 m. The incident neutrons are transported from the moderator by Ni-coated guide tubes
of rectangular shape with dimensions: 60 mm wide, 160 mm high and 100 m long. Resolution
of the NERA spectrometer within the energy transfer 5 – 100 meV is about 2-3% [6,7].

3. STRUCTURAL PHASE TRANSFORMATIONS IN SOLID MESITYLENE-D3.

The solid phases of partially deuterated mesitylene-D3, 1,3,5-(CH₃)₃C₆D₃ were studied
in more detail, because the intensity of the diffraction peaks was much stronger than for
mesitylene-D0, and the IINS spectra reflected dynamics of methyl groups. The typical NPD spectra measured for a scattering angle of 56.6°, after different freezing and cooling procedures, are presented in Figures 1-3. The intensity of scattered neutrons - I(\(\lambda\)), measured on a time-of-flight scale, is normalized to the flux of incident neutrons - \(\Phi(\lambda)\) measured by the same detectors on a standard vanadium sample. The time-of-flight scale has been transformed to the lattice spacing scale using the Bragg diffraction formula. For a better visualization of temperature effects, the NPD spectra are shifted by addition of some constants.

The liquid sample of mesitylene-D3, rapidly quenched in the liquid nitrogen bath, did not show any structural phase transitions up to 200 K. Repeated cooling and heating at a rate of 2K/min of this sample in the cryostat did not change the diffraction pattern in the temperature range of 20 K – 200 K either (see spectra 1 – 4 in Fig. 1). It seems that rapidly frozen samples of solid mesitylene present the same conglomerate of different crystallographic structures, which is quite stable up to 200 K. However, after subsequent heating and annealing of this sample at 220 K, the diffraction pattern of phase I has been recorded. Repeated cooling and heating do not change the diffraction pattern of phase I in the temperature range from 220 K to 20 K, as one can see in the spectra 5 and 6 of Fig. 1.

![Figure 1](image1.png)

**Figure 1.** The NPD spectra of a rapidly frozen and cooled sample of mesitylene-D3 recorded at subsequent heating and cooling processes.

The same sample, placed into cold cryostat shaft at room temperature and cooled down at a rate of 5 K/min, solidified as a mixture of phase I and phase II. The NPD spectra of such a solid sample of mesitylene-D3, measured during a heating procedure are presented in Fig. 2. Reversible structural phase transitions from phase III to II were detected at about 90 K, but the initial amount of phase I was stable. One can see that in this case transition from phase II to phase I occurs at 200K.

![Figure 2](image2.png)

**Figure 2.** The NPD spectra of mesitylene-D3 cooled down at 5K/min and recorded at a subsequent heating process.
After melting phase I in the cryostat and cooling down the liquid sample from 240K, at a rate of 2K/min, the undercooled liquid solidified in the structure of phase II, and at 20K we got a pure structure of the low temperature phase III. The NPD spectra presented in Fig. 3 illustrate the structural transformations of solid mesitylene, when the heating procedure starts at phase III. Transition III - II occurs just above 90K and is reversible with a small hysteresis of about 2-5K, when phase II was heated up to no more than 180K. After a few hours of annealing of the phase II at 200K, the NPD spectrum displayed some nucleation of phase I (see spectrum 4 in Fig. 3). Cooling the sample at such a state of transformation, the phase II can be undercooled down to 20K, without transition to phase III. Transition from phase II to phase I is not reversible, it starts at approx. 190K, but the NPD spectra indicated a mixture of phase II and phase I up to 210K. The pure phase I diffraction pattern was achieved only after annealing of the sample at 220K. Phase I does not undergo any structural transition at cooling down to 20 K (see spectra 5 and 6 in Fig.3), and can only be melted at T_m=227 K.

The NPD spectra 1 - 5, indicate structural phase transitions in mesitylene-D3 at heating from the low temperature phase III, spectra 5 and 6 confirmed the stability of phase I from 220 K down to 20 K.

The temperature dependence of the IINS spectra measured by heating of phase III are shown in Fig. 4. The time-of-flight spectra recorded at fifteen scattering angles between 20° and 160° were summed up to improve the statistics. The summed-up spectra were normalized to the same number of incident neutrons integrated over the range of neutron wavelengths from 0.5 Å to 6 Å, and corrected for background by measuring the empty cryostat.

Figure 3. The NPD spectra 1 - 5, indicate structural phase transitions in mesitylene-D3 at heating from the low temperature phase III, spectra 5 and 6 confirmed the stability of phase I from 220 K down to 20 K.

Figure 4. The corresponding IINS spectra measured by heating the phase III of solid mesitylene-D3. Note the QNS broadening of the elastic line for temperatures above the phase III to phase II structural phase transition.
The intensity of scattered neutrons is presented in arbitrary units, which approximately corresponds to a real intensity for 10 hours of measuring time. Typical measurement times for different phases at 20 K were 12-15 hours, while for the spectra at other selected temperatures ranged from 3 to 5 hours. The time-of-flight scale is transformed to the incident neutron wavelength using the quantum relation:

$$\lambda = \frac{h}{mv} = \frac{(h/mL)}{t},$$

where \(m\) and \(v\) are neutron mass and velocity, while \(L\) and \(t\) are the proper flight path length and time-of-flight, respectively.

The elastic line, which has a maximum at \(\lambda_0 = 4.25 \text{ Å}\), is not fully shown in the scale of figure 4. The shape of this line measured at 20K corresponds to the resolution function of the NERA spectrometer measured by elastic scattering on vanadium [6, 7]. It means that within the energy resolution of the 0.6 meV, stochastic motions of methyl groups are not observed in the solid phases of mesitylene at 20 K. Practically, we do not see rotational jumps of methyl groups in phase III at 80K as well. Significant quasi-elastic broadening (QNS) of the elastic line is observed above the phase III – phase II transition at about 90K. From the QNS broadening observed in phases II and I at temperatures above 100K one can conclude that the jump rate of methyl groups is of the order of phonon frequencies, i.e. in the THz range. These stochastic jumps cause strong anharmonic effects in the lattice and internal dynamics of mesitylene. As one can see in Fig. 4 (spectra 3, 4 and 5), the inelastic spectra are completely smeared out and cannot be used for the determination of the vibrational density of states.

The scheme of structural phase transformations observed in solid mesitylene, combining the results of recent NPD and IINS investigations of mesitylene-D3, is presented in Figure 5.

![Figure 5](image-url)

**Figure 5.** Scheme of phase transformations observed in mesitylene-D3.
4. SOLID PHASES OF MESITYLENE-D0 AND THEIR PHONON DENSITY OF STATES

Solid phases of mesitylene-D0 can be easily obtained using a proper thermal procedure according to the scheme of phase transformations presented in Figure 5. The structural modifications of solid mesitylene have been identified by their characteristic NPD patterns in the lattice spacing range of 0.5 – 0.7 nm. The characteristic diffraction patterns of the three structural modifications of solid mesitylene, which can be obtained at low temperatures, are displayed in Figure 6.

The IINS spectra measured at low temperatures exhibit peculiarities in the dynamics of these structural modifications of solid mesitylene. The difference in harmonic lattice dynamics of phases III and II, as well as the stochastic dynamics of methyl groups in these phases, are displayed in Figure 7. One can see that the QNS wings of phase II at 90K are much broader than those in phase III. This means that the barriers for methyl group rotations in phase II are much lower than in phase III. At higher temperatures, especially above the III – II transition at 91 K, the IINS spectra of phases II and I seem to be quite similar.

The temperature dependence of the IINS spectra of phase I is shown in Figure 8. The IINS spectrum of liquid mesitylene at 290 K displayed also in Fig. 8 is almost smooth and shows broad quasi-elastic wings caused by rotational and translational diffusion of molecules in the liquid phase. The QNS wings for solid phase I measured at 220 K are narrower, and probably they are caused only by rotational diffusion of methyl groups. There is no significant difference in the IINS spectra of phase I down to about 100 K. They show a few precursory peaks of internal vibrations of the molecule and still significant quasi-elastic scattering caused by relatively fast reorientations of methyl groups. Quasi-elastic scattering is not observed at 20 K. The IINS spectrum at this temperature reflects the harmonic dynamics of the lattice and internal vibrations of the molecule in the structure of phase I.

![Figure 6. The characteristic NPD spectra of solid phases of mesitylene-D0 measured at 20K.](image-url)
**Figure 7.** Comparison of the IINS spectra of the solid phases II and III of mesitylene-D0 measured at 20K and 90K.

**Figure 8.** The IINS spectra of solid phase I at T=20K, 120K and 220K and liquid mesitylene-D0 at T=290K.
Figure 9. Density of phonon states of the three structural modifications of solid mesitylene-D0 obtained from the IINS spectra at 20K.

The density of the phonon states $G(\nu)$, obtained within the approximation of harmonic dynamics and one-phonon scattering processes [8] from the IINS spectra of various phases of solid mesitylene at $T=20$K are presented in Fig. 9 in the energy range up to 40 meV. The intense bands seen in the spectrum of phase III at 19.2 meV and 23.3 meV, are interpreted as corresponding to librations of the methyl groups. These bands disappear in the spectra of phases II and I, which testifies a significant decrease of the barrier heights for rotation of the methyl groups in these phases. As a consequence, the libration of methyl groups are shifted into the energy range of lattice vibrations below 15 meV. The $G(\nu)$ of phase I at low energies is proportional to $\nu^2$, according to the Debye model of dynamics of ordered crystals. The $G(\nu)$ spectrum for phase II in the range of the lattice vibrations is characterized by broadened bands of optical phonons and much greater density of states in the acoustic phonon range below 10 meV. This additional density of states is known as the so-called "boson peak" in the $G(\nu)$ of disordered solids. The above evidence suggests that phase II could be classified as a reorientational or proton glass. The internal vibrations of the mesitylene molecule above 30 meV practically do not depend on the crystalline structure.

5. CONCLUSIONS

The NPD investigations of solid mesitylene at different temperatures give clear evidence of three different structural phases of crystalline mesitylene. The phase I, which can be obtained as a single phase only after annealing of solid mesitylene close to the melting point, is stable in the whole temperature range of solid phases. Much more often liquid mesitylene is solidifying in the structure of phase II, which at 91 K transforms to the low temperature phase III. This phase is characterized by the relatively high barriers for methyl rotations. The energy of librational modes in phase III has values of 19.2 and 23.3 meV, which are too high for effective slowing down of cold neutrons. In phases II and I the hindrance barriers of methyl
rotations seem to be weaker and the librational modes of methyl groups are shifted to the energy range of the lattice modes below 15 meV.

From the obtained IINS results we can conclude that due to the presence of methyl groups in the mesitylene molecules a number of rotational modes is added to the lattice modes of the solid phases I and II. It seems that phase II can be classified as a "protonic glass", because the density of phonon states $G(\nu)$ of this phase below 10 meV is softer than in phase I. The relatively high density of phonon states in phases I and II below 10 meV is promising from the point of view of using solid mesitylene as a cold moderator. The $G(\nu)$ spectra presented in Figure 9 can be used for calculations of neutron scattering cross-sections needed for optimization of an advanced cold neutron moderators [9].

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Inelastic neutron scattering and spectral measurements of advanced cold moderator materials

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ABSTRACT

Inelastic neutron scattering with emphasis on energetically low lying modes as well as cold neutron leakage measurements have been performed on four prospective advanced cold moderator materials. Employing the time-of-flight instrument SV29 at the Jülich FRJ-2 reactor, spectra have been obtained from synthetic methane clathrate, tetrahydro-furan (THF) clathrate, 1,3,5-trimethyl-benzene (mesitylene) and light water ice at several temperatures between 2 K and 70 K. Clearly separated excitations at energy transfers of ±1 meV, ±2 meV and ±3 meV have been observed with synthetic methane clathrate. In mesitylene a wealth of low lying excitations have been observed. In the quenched phase we found lines at 4.7, 7.2, 9.6, 13.6, 15.4, 18.4, 19.0, 23.0, 29.5 and 34.3 meV, respectively. In the annealed phase, we observed significant shifts with the majority of lines. The lowest lying lines now are located at 7.0, 8.5 and 10.5 meV, respectively. In hexagonal ice at T = 2 K up to now unreported low lying energy levels were found at energy transfers of 1.8 meV and 2.8 meV. An additional line at about 10 meV could be detected in THF clathrate. Mesitylene, synthetic methane clathrate and water ice, all at T = 20 K, have been tested as moderators at the Jülich spallation mock-up JESSICA. The expected gain in neutron leakage current at energies around 2 meV as compared to conventional liquid hydrogen moderators has been observed for methane clathrate and mesitylene.

1. INTRODUCTION

The motivation for the investigations described in this paper is the development of advanced cold neutron moderators in particular with respect to pulsed spallation sources. Solid methane at low temperatures, e.g. T = 20 K, is generally considered the best moderator medium for cold neutron sources [1], [2], [3]. In contrast to liquid hydrogen at the same temperature it experimentally exhibits a Maxwellian spectrum with a “neutronic” temperature of about 23 K. The observation that neutrons are virtually in thermal equilibrium with methane at this temperature is attributed to the low lying energy levels, which in turn are believed to be due to the free rotations of a limited number of methane molecules in the solid phase. In addition, methane has a 70 % higher proton density than liquid hydrogen (Table 1), which yields a much more efficient slowing down of fast neutrons. As a consequence of both properties of methane an intensity gain of a factor of 3 to 4 at neutron energies around 2 meV as compared to liquid hydrogen has been observed as can be seen from Fig. 1.
A not quite as perfect cold spectrum is observed with water ice at 20 K. On the other hand, ice shows an extended slowing down spectrum covering the so-called thermal neutron energy range (ambient temperature regime). This would entail narrower neutron pulse widths (better resolution for time-of-flight spectrometers) than those obtainable from common ambient temperature water moderators at pulsed neutron sources.

Therefore, a combination of methane and water ice at low temperatures could be the ideal moderator over a broad energy range from 2 meV up to, say, 100 meV. Indeed, there are inclusion compounds of gases or other molecules in water, the clathrates, which might exactly serve this purpose. A well-known example is methane clathrate, a substance, which even occurs on the deep sea floor. Unfortunately, it is only stable under these conditions (high pressure and/or low temperature). On the other hand, inelastic neutron scattering on a few samples of natural deep sea methane clathrates revealed the same low energy levels [4], which have been discovered long ago with solid methane [5].

![Figure 1. Comparison of measured cold neutron fluxes from various moderators [from ref. 1]](image)

Since the proper composition of natural methane clathrate is not predictable, we investigated the spectral properties of synthetic material approaching the nominal stoichiometric ratio of one methane molecule per 5.75 water molecules. The results of the inelastic neutron experiments are presented below.

Due to the difficulties with methane clathrate, it seems worthwhile, on the other hand, to search for easier to handle alternatives. In addition to simple operation parameters many methyl groups and/or high proton densities are usually necessary for good moderation performance. The relevant physical properties of a few candidate materials are compiled in Table 1. Due to the technical problems with the synthesis of methane clathrate (30 bars at 70 K), we also investigated a compound easier to produce, tetrahydrofurane (THF) clathrate. The room temperature liquid THF (C₄H₈O) and water mix easily and form an inclusion compound at 6°C. This hydrate, composed of one THF per 17 water molecules, can thereafter easily be cooled down to cryogenic temperatures. In order to complete our studies with respect to searching for low lying excitations in solid cryogenic moderator media we also measured water ice and mesitylene (1,3,5-trimethyl-benzene). The latter contains three methyl groups, which if unhindered to rotate may be the reason for the observed good moderation performance (compare Fig. 1).
Water ice may still be a candidate for pulsed sources for reasons described above. Furthermore, water ice not only is simple to produce, but at temperatures as low as 5 K has an extremely high thermal conductivity, which is important for removing the power deposited by the primary neutron source (nuclear heating). Unfortunately, it has recently been observed that the conductivity is drastically reduced by radiation defects [6].

Table 1. Physical parameters of selected cold moderator materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Density [g cm$^{-3}$]</th>
<th>Proton density [10$^{23}$ cm$^{-3}$]</th>
<th>Melting point [K] at 0.1 MPa</th>
<th>Boiling point [K] at 0.1 MPa</th>
<th>Thermal conductivity [W/m/K]</th>
<th>Radiation resistance</th>
<th>Simplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>0.47</td>
<td>0.70</td>
<td>90</td>
<td>164</td>
<td>0.4</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CH$_4$-hydrate</td>
<td>0.95</td>
<td>0.72</td>
<td>160**</td>
<td>- -</td>
<td>0.1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>H$_2$O-ice</td>
<td>0.93</td>
<td>0.62</td>
<td>273</td>
<td>373</td>
<td>150*</td>
<td>--</td>
<td>+</td>
</tr>
<tr>
<td>THF-hydrate</td>
<td>0.90</td>
<td>0.60</td>
<td>278</td>
<td>(373)</td>
<td>0.05</td>
<td>--</td>
<td>+</td>
</tr>
<tr>
<td>mesitylene</td>
<td>0.87</td>
<td>0.44</td>
<td>220</td>
<td>437</td>
<td>?</td>
<td>+ + ?</td>
<td>+ + +</td>
</tr>
</tbody>
</table>

THF (tetrahydrofurane, C$_4$H$_8$O); Mesitylene (1,3,5-trimethyl-benzene); * at T = 5 K; ** stability limit.

2. EXPERIMENTAL

2.1 Sample preparation

Methane clathrate has been produced in a high pressure reaction chamber at a temperature in the vicinity of 273 K; the first part of the reaction took place slightly below the ice melting point, the second part of the reaction slightly above. The reaction chamber has been pressurized with methane gas of 60 bars. Water had been sprayed through narrow nozzles into the cooled chamber. The clathration reaction lasted for 48-72 hours, yet most of the transformation took place in the first hours of reaction. Subsequently, the product has been removed and stored at liquid nitrogen temperatures. Details of the procedure are published elsewhere [7]. The important point is that the production scheme for methane clathrate developed in Göttingen not only yields the desired quality with respect to the microscopic properties, but also is suitable for mass production.

The latter is of utmost importance for a real cold neutron source, where amounts of the order of one liter are required for the moderator volume proper and another 10 to 20 liters for the necessary loop. In fact, for the moderator experiments described below, about 900 g of this compound were used. Tetrahydro-furane (THF) clathrate has been formed by mixing water and THF at room temperature in a mass ratio of 17 water molecules per one THF molecule and cooling the solution to below 6°C, where it solidifies. In order to obtain pellets, the solution was dripped into liquid nitrogen. Ice as well as solid mesitylene have been produced by simply cooling the room temperature liquids below their freezing points, respectively. With mesitylene we have applied two different cooling rates in order to obtain different crystallographic structures, which are believed to influence the rotational freedom of the methyl groups [8].
2.2 Inelastic neutron scattering

The experiments have been conducted at the time-of-flight spectrometer for thermal neutrons, SV29 at the FRJ-2 reactor. In order to find the respective optimum range for energy transfer with simultaneously obtaining the required energy resolution, the measurements have been performed with three different incoming energies, 7 meV, 26 meV and 41 meV and various scattering angles. Samples have been measured with flat aluminium vessels, 3 cm by 7 cm wide and 0.1 and 0.2 cm thick, the latter used for the granular methane clathrate. Measurements have been performed between 2 K and 70 K using a closed cycle cryostat. A distinct separation from the elastic line of the expected lowest energy levels of the order of meV (e.g. for methane clathrate, ±1 meV, +2 meV and +3 meV) was possible with 7 meV, as can be seen in Fig. 2.

2.3 Cold neutron leakage current measurements

In order to assess the different performances of methane clathrate, ice and mesitylene moderators, respectively, we have performed neutron leakage current measurements at the Jülich spallation source mock-up JESSICA. The measurement of the leakage spectrum of THF clathrate has not been included in these studies so far. We have used the same moderator vessel for the three media quoted above. Therefore the results do not necessarily provide information on the optimum performance of the investigated materials. In the experiments 1 µs long pulses of 1.3 GeV protons are deposited into a 70 liter mercury target and the fast neutrons generated in and emitted from this target are partly intercepted and slowed down in the adjacent moderator materials. The volume of the moderator vessel is of the order of one liter with the dimensions 15×12×5 cm³ (width×height×thickness). The largest face of the vessel is viewed by the neutron detector located about 5 m from the moderator. The media are cooled down to 20 K by a closed cycle refrigerator. The energy distribution of the slow neutrons leaking from the moderator is measured by a time-of-flight technique and transformed to the energy afterwards. Background is measured by placing a boron carbide (B₄C) absorber in the neutron flight path and these data subtracted from the leakage current data. The JESSICA and cryogenic installations, respectively, are described in more detail elsewhere [9], [10].

3. RESULTS

3.1 Inelastic neutron scattering

3.1.1 Synthetic methane clathrate

The inelastic spectra from synthetic methane clathrate taken at five different temperatures between 5 K and 70 K are shown in Fig. 2. With an incoming neutron energy of 7 meV a clear separation of the expected lowest rotational levels for methane clathrate (±1 meV, +2 meV and +3 meV) from the elastic line was possible with. It should be noted that at the highest temperature of 70 K, the discrete lines of the free rotations are smeared out to a quasi-elastic line due to diffusional motions. The energies of the observed lines at the lowest temperature corresponds perfectly to the lines found with natural deep sea methane clathrate [4].
3.1.2 Tetrahydro-furane (THF) clathrate

The spectrum from THF clathrate is shown in Fig. 3. It exhibits a feature at about $\Delta E = 10$ meV not present in pure ice (compare Fig. 5 below) and therefore attributed either to the THF molecule embedded in the ice or to the different crystalline structure of the inclusion compound. With improved resolution due to the lower incoming neutron energy of 7 meV we investigated the lowest energy transfer regime. The results are shown in Fig. 4. The observed peaks at energy transfers of about 1.8 meV and 2.8 meV, respectively, we have observed in ice as well.
Figure 4. Inelastic spectra at the lowest energy transfers from THF clathrate at $T = 2$ K and for three scattering angles ($E_0 = 7$ meV, $\delta E = 0.4$ meV; $Q_o = 1.5; 1.9$ and $2.9$ Å$^{-1}$ resp.).

3.1.3 Hexagonal ice

The results for hexagonal ice, which is usually obtained by cooling down light water slowly to cryogenic temperatures, are shown in Figures 5 and 6 for different energy transfer regimes, respectively, but at a temperature of $2$ K in both cases. To our knowledge there has been no report in the literature about an observation of these low energy modes in ice. The physical origin of these excitations is not understood yet.

Figure 5. Inelastic spectra from ice at $T = 2$ K and for two scattering angles ($E_0 = 41$ meV, $\delta E = 4$ meV; $Q_o = 4.8$ and $7.2$ Å$^{-1}$ resp.). Note that the line at $10$ meV observed with THF clathrate is missing in ice (comp. Fig. 3).
3.1.4 Mesitylene

It has been observed that mesitylene forms different low temperature crystalline modifications depending on the rate of cooling [11]. The crystalline phase obtained by slowly cooling down (at a rate of 1 to 2 K per minute only) is supposed to form a structure with high barriers against free rotations of the methyl groups. This assumption should be visible in different differential inelastic neutron cross sections. Therefore we performed scattering experiments from a quenched mesitylene specimen as well as one, which was subject to a particular cooling and annealing treatment suggested elsewhere [8]. The results are shown in Figure 7.

**Figure 7.** Inelastic spectra from mesitylene at T = 2 K. Circles denote data taken with the quenched sample, and crosses taken with the sample annealed for 8 hours just below the melting point and cooled down slowly afterwards. \( E_0 = 26 \text{ meV}, \delta E = 2.1 \text{ meV}; Q_o = 3.0 \text{ and } 5.8 \text{ Å}^{-1}, \text{respectively}. \)
3.2 Moderator performance

The results obtained with JESSICA spallation neutron source mock-up are shown in Fig. 8. The data have to be considered preliminary, because no shape and size optimizations of the moderator vessel have been attempted so far. The only correction applied to the spectra in Fig. 8 is the normalization to the same mass densities of the moderator materials. However, increased intensity compared to ice for methane clathrate and mesitylene at energies below about 5 meV is evident. Compared to mesitylene, on the other hand, methane clathrate exhibits increased intensity in the thermal energy range as expected due to the existence of the ice host (compare section 1). Due to the low statistical accuracy of the present data for energies below about 3 meV and the missing geometrical moderator optimization a decision upon the superiority of either the clathrate or mesitylene can not be made at this point.

4. CONCLUSIONS

Synthetic methane clathrate has been found to exhibit the rotational energy levels of solid methane rendering it the potentially optimum cold moderator material, because it combines the excellent slowing down properties of solid methane at the lowest energies with those from water ice at thermal energies. So far unknown energy levels close to those observed with methane have been detected in ice suggesting that they are responsible for the comparatively good slowing down properties of this material. The same energy levels as in ice have been found in THF clathrate as well as an additional line at 10 meV. Whether this line has any importance for an improved moderation behavior of THF clathrate is not known yet, because cold neutron spectra have not been measured so far.

Figure 8. Energy distribution of cold neutrons emitted from ice, mesitylene and methane clathrate moderators, respectively, measured at the Jülich spallation source mock-up JESSICA. The enhancement of the intensity compared to ice at the lowest energies attributed to methane in the clathrate as well as the methyl groups in mesitylene is clearly seen.
The wealth of low lying energy levels of mesitylene may well explain the favorable spectra observed already in the past as well as in the present investigations. Due to the intriguing simplicity in handling the room temperature liquid, mesitylene has to be considered a serious candidate material for an advanced cold neutron source. Simplicity may play another important role with respect to heat deposition in any of these materials in a future multi megawatt spallation neutron source. Any of the materials investigated in this study have to be in granular form. Pellets can be easily produced from substances, which are liquid at room temperature like water, mesitylene or THF-clathrate. Methane clathrate has been produced as pellets for these experiments, and it does not seem to be impossible to extend the scheme used here to a real mass production.

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Methane Pellet Moderator Development

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ABSTRACT

A methane pellet moderator assembly consisting of a pelletizer, a helium cooled sub-cooling tunnel, a liquid helium cooled cryogenic pellet storage hopper and a 1.5L moderator cell has been constructed for the purpose demonstrating a system for use in high-power spallation sources.

DESCRIPTION OF THE SYSTEM

The pelletizer, cooled by liquid nitrogen, forms and releases 30,000 2.7mm methane pellets by reverse sublimation in a honeycomb panel in a 50 minute cycle. Figure 1 is a photograph of the 0.15m x 0.9m 3mm cell honeycomb freezing panel; the circle inset shows the honeycomb matrix magnified. The pelletizer contains two honeycomb panels.

Figure 1. The honeycomb freezing panel; the inset shows the honeycomb matrix in detail.
Figure 2. The methane pelletizer, mounted in a foam insulated chamber above the cryogenic conveyor/sub-cooling tunnel assembly. The liquid nitrogen circulator is to the right. The pellets are conveyed slowly through the tunnel on a metal belt, allowing time to sub-cool.

Figure 3. Methane pellets on the conveyor belt entering the sub-cooling tunnel.
After passing through the sub-cooling tunnel, the pellets drop into and are stored in a liquid helium cooled hopper. The photo shows the cryogenic hopper/valve assembly (with the vacuum jacket removed) mounted below the end of the conveyor. The window in the center of the hopper is where photographs of the pellets in the hopper are taken.

Figure 4. The cryogenic hopper/valve assembly (with the vacuum jacket removed).
Figure 5. The cryogenic hopper filled to the 1.3-liter level with methane pellets.

If progress is made in collecting the pellets at a low enough temperature so that they do not agglomerate in the hopper, the pellets in the hopper will be transferred through the middle and lower ball valves and into the mock moderator cell via a 25mm id transfer line. When required, the moderator cell will be emptied by flash melting the pellets using pressurized methane gas and then blowing the liquid methane from the cell.

PROGRESS

The liquid nitrogen cooled pelletizer works well, growing batches of 30,000 pellets in 25 minutes, followed by a low pressure defrost/release cycle. The conveyer and freezing tunnel function well, however sub-cooling the pellets sufficiently to produce a non-sticky, fluid medium has not yet been fully realized. Pre-cooling the system to 40K followed by a low pressure (5 Torr) defrost has produced the Adriest@ pellets. These pellets were dry enough to flow and fill the hopper with 1.3 liters of pellets (two batches). However, the pellets then agglomerated, so that the hopper could not be emptied into the moderator. A liquid helium-cooled cryopump is being added to the tunnel to further reduce the defrost pressure (~10^-2 Torr) which should reduce the temperature of the pellets during the defrost cycle from 70 K to about 50K. It is presumed that the colder pellets will be less likely to stick together.

ACKNOWLEDGEMENT

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Figure 6. The 1.5 liter Amock moderator assembly (with the vacuum jacket removed).
Study of radiation effects in hydrogenous moderator materials at low temperatures (URAM-2 project)

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1. INTRODUCTION

The goal of the URAM-2 project was to study fast neutron irradiation effects in solid methane, water ice, and methane hydrates which are of crucial importance for a design of cold moderator of the ESS target station. Later on, tetrahydrofuran (THF) hydrate was added to be studied because it is a material easy to be manipulated with. The URAM-2 programme was expected to give knowledge about possibility of burping in ESS cold moderator beads, temperature rise in burps, and maximum allowable residence time of beads until burping.

Results obtained on accomplishment of the program are presented in this report. Preliminary research and development of a cryogenic irradiation facility at the channel N° 3 of the IBR-2 reactor have taken two years (1999-2000). In 2001, the URAM-2 irradiation facility has been constructed, tested, and mounted to the working position near the IBR-2 reactor. The irradiation rig consists of three principal parts: - irradiation rig head, charging device, and cooling system. It enables to irradiate either previously prepared pelletized samples, or to make samples by condensing gas into irradiation cavity. Description of the facility and the project plan were reported earlier [1, 2]. Irradiation experiments were started on November 13, 2001 and finished May 22, 2002.

2. SUMMARY OF THE RESULTS AND ANALYSIS.

2.1 Solid methane

27 runs of irradiation with 11 types of samples (layers of methane with thickness from 0.28 mm up to 5 mm condensed onto the walls of the chamber and spherical segments of 4.6, 7.5, 9, and 14.3 mm height) were performed. Irradiation time was from 3 hours up to 26 hours.

Main results:
Only one spontaneous burp occurred (in 5 mm shell sample after 11 hours). No other spontaneous burp was observed even for bigger samples and longer irradiation. For irradiation time ≥ 4 hours and for size of samples ≥ 1 mm thermally induced burps were always registered; the smallest sample 0.3 mm displayed a burp once of two attempts. Maximal rate of energy accumulation in solid methane (at temperatures more than 20K) was estimated to be as high as 1.6±0.2% of absorbed dose rate, that is, ~32mW/g for ESS dose rate of 2 W/g. Saturated stored energy was observed to be dependent on irradiation temperature (as it was predicted based on previous experience with solid methane irradiation) and was estimated to be as high as 110-30 J/g in the range 21-28K.

Basing on a comparison analysis of URAM-2 results and experience with solid methane moderators of IPNS, IBR-2, and KENS facilities, conclusion is made that for irradiation tempera-
ture <28K spontaneous burps are expected in a single bead of ESS moderator (with liquid hydrogen cooling, 2 W/g absorbed dose rate), as for such condition, saturated concentration of radicals is less than critical concentration. Simplified analysis resulted in high probability of propagation of a burp from one beads of solid methane to another, but this conclusion may not be considered as fully proved. Maximum allowable residence time of beads in the ESS solid methane moderator estimated on occurrence of burping, is 30 - 50 min depending on maximal temperature of beads.

2.2 Water ice

22 runs of irradiation with 4 types of samples (spherical segments of 3, 7.5 and 15 mm height and beads of ice in argon matrix) were performed. Irradiation time was from 3 to 20 hours.

Main results:
Spontaneous burps were observed for all bulky, at temperature <35 K, regardless a size of a sample. Time and stored energy in spontaneous burps have a stochastic nature; time varied from 5 till 20 hours. Evidence of inverse relation between thickness of sample and critical amount of stored energy was observed for samples less than 8 mm. For bigger samples there was no such relation. For irradiation time 3 hours and more thermally induced burps were always registered. Saturated or maximal stored energy was observed to be only slightly dependent on irradiation temperature in the range 19-42K and was estimated to be 148-110 J/g. Maximal rate of energy accumulation in water ice was estimated to be as high as 5.4%±0.4% of absorbed dose rate, that is, ~50 mW/g for ESS dose rate of 1 W/g. For irradiation temperature <35 K-36 K, probability and periodicity of spontaneous burps depends on irradiation temperature and on methods of fabrication of a sample. For irradiation temperature >35K-36K and for any duration of irradiation, no spontaneous burp is expected in a single bead of ice of ESS moderator as saturated concentration of radicals is less than critical concentration. Recommended values of maximum allowable residence time of ice beads in the ESS ice moderator (if ice beads are prepared by slow freezing, not in liquid nitrogen) at 20-35 K vary from 35 min to ~ 2 h depending on temperature.

2.3 THF hydrate

4 runs of irradiation of samples in the form of a hemisphere of 15 mm height were performed. Irradiation time was from 4 hours to 15 hours.

Main results:
Radiation effects in THF hydrate are similar to that of pure water ice but with lower rate of energy accumulation. Spontaneous burping was observed after 13 hours of irradiation at irradiation temperature 20 - 30 K. Maximal rate of energy accumulation in THF was estimated to be no more than 2.4% of absorbed dose rate, that is, ~23mW/g for ESS dose rate of 1 W/g. Recommended values of maximum allowable residence time of THF hydrate beads at 20 K are 1.5 hours.

2.4 Hydrate of methane

4 runs of irradiation of samples in the form of beads 2-4 mm in argon matrix (7 cm³) were performed. Irradiation time was from 5 hours to 24 hours.
Main results:
Radiation effects in methane hydrate are very similar to that of THF hydrate. Spontaneous burping was observed after 13 hours of irradiation at irradiation temperature 20 - 25 K. There were no spontaneous burps at T > 25 K. Recommended values of maximum allowable residence time of methane hydrate beads at 20 K are 1.5 hours.

3. URAM-2 CRYOGENIC IRRADIATION FACILITY

Brief description of the facility. The facility consists of four main parts (Fig. 1):

charging device;
irradiation rig head;
liquid helium cooling system;
measuring system.

As is shown in the Fig. 1, the head part is connected to charging device by a transport tube, which allows to load or to unload samples. Through the helium pipeline, helium is delivered from liquid helium Dewar vessel to the sample situated inside irradiation rig head and then it is collected in a gas accumulated vessel. Electric placed communication lines and PC intend for collecting data during an experiment. The head part and terminal part of the helium pipelines are placed into an evacuated jacket with high vacuum. The keeping of high vacuum is utterly necessary to avoid wall heat load to the helium and to the samples. There is a beryllium reflector set behind the head part of the rig. It was done to increase fast neutron flux with better isotropy.

**Figure 1.** General schematic view of irradiation facility “URAM-2”:
(1) the IBR-2 reactor; (2) head part of the facility; (3) transport passage, helium pipelines and electric communications; (4) charging device; (5) shielding plug on rails; (6) liquid helium Dewar vessel; (7) gas containers; (8) PC with communications; (9) rails
The charging device scheme could be found in Fig 2.

**Figure 2.** Conceptual design of the URAM-2 irradiation facility:
(1) the IBR-2 reactor; (2) irradiation capsule; (3) carrying bowl with a cart in ‘near of the reactor’ position; (4) helium pipelines; (5) evacuated transport passage; (6) nitrogen cryostat; (7) carrying bowl with a cart in ‘out of the reactor’ position; (8) charging tube with plug; (9) vacuum lock

Before beginning of a sample preparation it is necessary to cool the irradiation cavity down to about 100 K. After it was done it is possible to charge materials have to be irradiated. They could be loaded by two ways: by charging beads of ice previously prepared or by condensing any gas into the irradiation cavity. To remove a sample from the irradiation cavity, the helium supply is closed and the sample is melted and evaporated by reactor heat. Then the irradiation capsule and evacuated transport passage are pumped. The head part of the facility is shown in Fig. 3.

**Figure 3.** Head part of the facility:
(1) Copper capsule; (2) thermal bridge; (3) a helium tube (heat exchanger); (4) thermocouples; (5) blue color marks solid methane, condensed onto the capsule inner surface.
Irradiation cavity inside the capsule has hemispherical shape with walls made of pure, oxygen-free copper (M1 purity of Russian standard, thermal conductivity 1000 W/m/K at 20K). The square of irradiation cavity is about 22 cm$^2$ and the inner volume is about 12 cm$^3$. The capsule is thermally insulated having a long neck of thin steel with a bellows. Total external heat (coming in through the neck and from the vacuum jacket walls) was estimated to be and really is ~1 W. A helium heat exchanger consists of four spires of a copper tube of 3 mm in diameter soldered onto a cylindrical wall of the capsule. Nuclear internal heat in the wall is about 2 W. Together with heat in samples and heat loads on helium guide tubes, the total heat load is about 4.5 W.

The cooling system of the facility is based on liquid helium, which is supplied from a Dewar vessel of 100 l capacity Fig. 1 (6) through the helium pipeline (3) to the irradiation capsule Fig 3. Then through another tube helium is collected in gas accumulated vessel. With such cooling equipment it is easy to keep temperature of a sample constant during an irradiation. The variation of the temperature during an irradiation does not exceed 0.5 K. The liquid helium from a big Dewar is considered to be the most effective coolant from an economical point of view. 100 l Dewar is enough to work at temperature 20K for about 24 hour.

Temperature monitoring by thermocouples and PC with frequencies 1.25 and 5Hz are arranged at 5 points: one thermocouple is installed inside the capsule at a distance of 8 mm from the bottom, two - at the outer surface of the capsule, and two of them measured temperature of input and output of cooling helium. Gas pressure monitoring is arranged with two gauges: 0-400 mbar, 0.1% accuracy at full scale, and 0-2 mbar, about 20% accuracy. The helium consumption is measured by two flow meters 0-3 m$^3$/hour, 3% accuracy and 0.5-5 m$^3$/hour, with accuracy 0.2%.

3.1 Main parameters of the URAM-2 facility
- fast neutron flux - 3 $10^{12}$ n/cm$^2$/sec;
- absorbed dose rate: induced by $\gamma$ - about 20 Gy/sec, by neutron in water - about 90 Gy/sec;
- maximal time of irradiation: about 24 hour at temperature 20 K;
- temperature range: 10 K ÷ 60 K
- possible sample material: any gases, low-boiling liquids.

More information about facility URAM-2 and absorbed dose rate could be found in [15,16]

4. OVERALL EXPERIMENTAL DATA OF IRRADIATION RUNS

Data on all irradiations done are summarized in Tables 1 and 2, including four additional irradiations with solid methane and ice samples (## 2.5, 2.10, 2.14, and 2.15), which were performed after ACoM-6 presentation, and appeared to be important for final analysis.

In Appendix one can find temperature and pressure diagrams during some selected burps, both spontaneous and induced. Number of an experiment in title of diagrams corresponds to its number in the Tables.
Table 1. Data of irradiation of methane samples

<table>
<thead>
<tr>
<th>No. of experiment</th>
<th>date</th>
<th>time of irradiation (hours)</th>
<th>shape &amp; size of a sample, (mm)</th>
<th>mass (g)</th>
<th>$T_{\text{irradiation min/max}}$ (K)</th>
<th>$T_{12}$ (before/after burps), (K)</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.11.01</td>
<td>6.0</td>
<td>a layer, 1.0</td>
<td>1.0</td>
<td>21.6/21.8</td>
<td>32/36</td>
<td>slow burp</td>
</tr>
<tr>
<td>2</td>
<td>15.11.01</td>
<td>6.0</td>
<td>a layer, 2.2</td>
<td>2.0</td>
<td>21.6/22.0</td>
<td>33.0/58.0</td>
<td>induced</td>
</tr>
<tr>
<td>3a</td>
<td>16.11.01</td>
<td>6.0</td>
<td>a layer, 0.28</td>
<td>0.3</td>
<td>21.6</td>
<td>–</td>
<td>no burp</td>
</tr>
<tr>
<td>3b</td>
<td>16.11.01</td>
<td>6.0</td>
<td>the same sample, 0.3</td>
<td>0.3</td>
<td>21.6</td>
<td>31.0/55.7</td>
<td>induced</td>
</tr>
<tr>
<td>4</td>
<td>16.11.01</td>
<td>4.0</td>
<td>segment, 4.6</td>
<td>0.6</td>
<td>21.6/23.0</td>
<td>–</td>
<td>no burp</td>
</tr>
<tr>
<td>5</td>
<td>20.11.01</td>
<td>6.0</td>
<td>segment, 7.5</td>
<td>1.2</td>
<td>22.0/25.0</td>
<td>31.0/56.0</td>
<td>induced</td>
</tr>
<tr>
<td>6</td>
<td>21.11.01</td>
<td>14.5</td>
<td>a layer, 0.28</td>
<td>0.3</td>
<td>21.6</td>
<td>–</td>
<td>slow burp</td>
</tr>
<tr>
<td>7</td>
<td>22.11.01</td>
<td>3.0</td>
<td>a layer, 1.3</td>
<td>1.3</td>
<td>10.0</td>
<td>24.0/56.0</td>
<td>induced</td>
</tr>
<tr>
<td>11</td>
<td>12.12.01</td>
<td>10</td>
<td>segment, 9.0</td>
<td>1.5</td>
<td>21.0/26.0</td>
<td>32.0/60.0</td>
<td>induced</td>
</tr>
<tr>
<td>12</td>
<td>12.12.01</td>
<td>10</td>
<td>the same sample, 1.5</td>
<td>1.5</td>
<td>65/70</td>
<td>–</td>
<td>measurement of $H_2$ release</td>
</tr>
<tr>
<td>13</td>
<td>13.12.01</td>
<td>4.25</td>
<td>segment, 4.6</td>
<td>0.6</td>
<td>15/17</td>
<td>32/50</td>
<td>induced</td>
</tr>
<tr>
<td>14</td>
<td>13.12.01</td>
<td>4.17</td>
<td>the same, 0.6</td>
<td>0.6</td>
<td>18.0/20.0</td>
<td>28.0/56.0</td>
<td>induced</td>
</tr>
<tr>
<td>15</td>
<td>13.12.01</td>
<td>3.0</td>
<td>the same, 0.6</td>
<td>0.6</td>
<td>21.0/23.0</td>
<td>–</td>
<td>no burp</td>
</tr>
<tr>
<td>16</td>
<td>13.12.01</td>
<td>3.0</td>
<td>the same, 0.6</td>
<td>0.6</td>
<td>24.0/26.0</td>
<td>–</td>
<td>no burp</td>
</tr>
<tr>
<td>17</td>
<td>13.12.01</td>
<td>6.0</td>
<td>the same, 0.6</td>
<td>0.6</td>
<td>24.0/26.0</td>
<td>32/59</td>
<td>induced</td>
</tr>
<tr>
<td>18</td>
<td>14.02.01</td>
<td>8.3</td>
<td>segment, 4.6</td>
<td>0.6</td>
<td>15.0/18.0</td>
<td>22.0/66.0</td>
<td>Induced</td>
</tr>
<tr>
<td>19</td>
<td>15.01.02</td>
<td>11.0</td>
<td>segment, 4.6</td>
<td>0.6</td>
<td>15.0/18.0</td>
<td>26/68.5</td>
<td>Induced</td>
</tr>
<tr>
<td>20</td>
<td>21.01.02</td>
<td>4.5</td>
<td>a layer, 1.3</td>
<td>1.3</td>
<td>11.0/13.0</td>
<td>–</td>
<td>no burp</td>
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<tr>
<td>21</td>
<td>22.01.02</td>
<td>20.0</td>
<td>a layer, 1.3</td>
<td>1.3</td>
<td>–</td>
<td>35.0/57.0</td>
<td>variable temperature (18-24 K)</td>
</tr>
<tr>
<td>22</td>
<td>24.01.02</td>
<td>8.5</td>
<td>a layer, 1.3</td>
<td>1.3</td>
<td>25.0/26.0</td>
<td>35.0/47.0</td>
<td>Induced</td>
</tr>
<tr>
<td>23</td>
<td>25.01.02</td>
<td>11.9</td>
<td>segment, 14.3</td>
<td>3.3</td>
<td>19.0/28.0</td>
<td>30.0/67.0</td>
<td>Induced</td>
</tr>
<tr>
<td>47</td>
<td>19.03.02</td>
<td>22</td>
<td>a layer, 1.5</td>
<td>1.5</td>
<td>21.5</td>
<td>26.7/71.3</td>
<td>Induced</td>
</tr>
<tr>
<td>48</td>
<td>21.03.02</td>
<td>10</td>
<td></td>
<td>1.5</td>
<td>21.5</td>
<td>27.6/62.7</td>
<td>Induced</td>
</tr>
<tr>
<td>2.14</td>
<td>22.01.03</td>
<td>11.12</td>
<td>a layer, 5.0</td>
<td>4.17</td>
<td>20-23</td>
<td>27/73</td>
<td>Spontan.</td>
</tr>
<tr>
<td>2.15</td>
<td>11.02.03</td>
<td>26.0</td>
<td>a layer, 2.8</td>
<td>2.6</td>
<td>20-21</td>
<td>30/87</td>
<td>Induced</td>
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Table 2. Data of irradiation of ice and hydrate samples

<table>
<thead>
<tr>
<th>No. of experiment</th>
<th>date</th>
<th>time of irradi. (hours)</th>
<th>T (K) irradiation min/max</th>
<th>sample</th>
<th>T8/T12 (K) ignition</th>
<th>T12, max</th>
<th>comments</th>
</tr>
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<tbody>
<tr>
<td>24</td>
<td>12.02.02</td>
<td>5</td>
<td>21/23.5</td>
<td>hemisphere ice</td>
<td>–</td>
<td>160</td>
<td>spontaneous burp</td>
</tr>
<tr>
<td>25</td>
<td>12.02.02</td>
<td>10.4</td>
<td>30/32</td>
<td>– / –</td>
<td>–</td>
<td>187.4</td>
<td>spontaneous</td>
</tr>
<tr>
<td>26</td>
<td>13.02.02</td>
<td>12.23</td>
<td>40/42.6</td>
<td>– / –</td>
<td>51/56</td>
<td>174.3</td>
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<tr>
<td>27</td>
<td>13.02.02</td>
<td>4</td>
<td>30/33</td>
<td>– / –</td>
<td>43.5/6</td>
<td>137.9</td>
<td>sample melted</td>
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<tr>
<td>28</td>
<td>14.02.02</td>
<td>7</td>
<td>31/32</td>
<td>– / –</td>
<td>39.5/46.2</td>
<td>167.7</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>14.02.02</td>
<td>5.33</td>
<td>17/20</td>
<td>– / –</td>
<td>23.5/25.2</td>
<td>169.2</td>
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<tr>
<td>30</td>
<td>14.02.02</td>
<td>10.0</td>
<td>25/28</td>
<td>segment 7.5 mm, ice 2.2 g</td>
<td>32/35</td>
<td>194</td>
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</tr>
<tr>
<td>31</td>
<td>15.02.02</td>
<td>11.0</td>
<td>20/23</td>
<td>– / –</td>
<td>26.3/26.6</td>
<td>193.2</td>
<td>new sample</td>
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<tr>
<td>32</td>
<td>16.02.02</td>
<td>3.0</td>
<td>20/23</td>
<td>– / –</td>
<td>28.6/34.3</td>
<td>134.5</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>16.02.02</td>
<td>5.0</td>
<td>39/41.4</td>
<td>– / –</td>
<td>51.5/57.5</td>
<td>140.7</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>16.02.02</td>
<td>3.33</td>
<td>40/41</td>
<td>– / –</td>
<td>–</td>
<td>61</td>
<td>no burp</td>
</tr>
<tr>
<td>35</td>
<td>16.02.02</td>
<td>10.5</td>
<td>19/23.5</td>
<td>– / –</td>
<td>–</td>
<td>191.5</td>
<td>spontaneous</td>
</tr>
<tr>
<td>36</td>
<td>35</td>
<td>13.03.02</td>
<td>5.3</td>
<td>22/27</td>
<td>– / –</td>
<td>32.3/35.1</td>
<td>159.1</td>
</tr>
<tr>
<td>37</td>
<td>13.03.02</td>
<td>5.0</td>
<td>35/37</td>
<td>– / –</td>
<td>45.7/50.3</td>
<td>140.1</td>
<td></td>
</tr>
<tr>
<td>2.5(1)</td>
<td>03.12.02</td>
<td>6.25</td>
<td>25.1/26.1</td>
<td>Segment 8.3 mm, ice 2.5 g</td>
<td>25.7/28.9</td>
<td>155.7</td>
<td>spontaneous</td>
</tr>
<tr>
<td>2.5(2)</td>
<td>04.12.02</td>
<td>8.62</td>
<td>25/26</td>
<td>– / –</td>
<td>25.5/29.6</td>
<td>167.4</td>
<td>spontaneous</td>
</tr>
<tr>
<td>2.5(3)</td>
<td>04.12.02</td>
<td>7.48</td>
<td>24.4/27.4</td>
<td>– / –</td>
<td>26/30</td>
<td>161</td>
<td>spontaneous</td>
</tr>
<tr>
<td>2.10</td>
<td>11.12.02</td>
<td>19.67</td>
<td>24.5/26.5</td>
<td>Segment 3 mm ice (0.4 g)</td>
<td>24.3/26.9</td>
<td>127.1</td>
<td>spontaneous</td>
</tr>
<tr>
<td>38</td>
<td>20.02.02</td>
<td>12.8</td>
<td>26/29.4</td>
<td>ice beads d=5mm, in Ar</td>
<td>32.5/33.5</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>21.02.02</td>
<td>4.16</td>
<td>20/26.9</td>
<td>hemisphere THF hydrate</td>
<td>– / 30</td>
<td>96.9</td>
<td>slow burp</td>
</tr>
<tr>
<td>40</td>
<td>21.02.02</td>
<td>14.5</td>
<td>20/29.3</td>
<td>– / –</td>
<td>29/31</td>
<td>169</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>14.03.02</td>
<td>12.91</td>
<td>20.4/29.6</td>
<td>– / –</td>
<td>–</td>
<td>160.0</td>
<td>spontaneous</td>
</tr>
<tr>
<td>42</td>
<td>14.03.02</td>
<td>7.0</td>
<td>30.4/38</td>
<td>– / –</td>
<td>60/64</td>
<td>~126</td>
<td>slow burp</td>
</tr>
<tr>
<td>43</td>
<td>14.03.02</td>
<td>5.25</td>
<td>20/25</td>
<td>methane hydrate beads in Ar</td>
<td>–</td>
<td>61.0</td>
<td>slow burp</td>
</tr>
<tr>
<td>44</td>
<td>14.03.02</td>
<td>13.0</td>
<td>20/25</td>
<td>– / –</td>
<td>–</td>
<td>81</td>
<td>spontaneous</td>
</tr>
<tr>
<td>45</td>
<td>17.05.02</td>
<td>24</td>
<td>30/35</td>
<td>– / –</td>
<td>–</td>
<td>142</td>
<td>a few argon near T12</td>
</tr>
<tr>
<td>46</td>
<td>23.05.02</td>
<td>21.15</td>
<td>25/29</td>
<td>– / –</td>
<td>30/30</td>
<td>82.4</td>
<td></td>
</tr>
</tbody>
</table>
5. METHODS OF PROCESSING OF RAW EXPERIMENTAL DATA

There are two values which have to be estimated from experimental data of burps, namely: energy release in a burp per gram of a sample, $Q_V$, and temperature of «ignition», $T_{ign}$. As to the second value, there was no problem to get it known as duration of a burp is always short - from 0.4 to 2 sec. Energy release in a burp was estimated by four different ways:

- for thin layer of methane $Q_V$ can be estimated by making balance of energy within 1 sec after ignition of a burp assuming adiabatic character of heating of a sample and copper walls of the chamber (that is, neglecting helium cooling as only small portion of energy is removed by a coolant during a burp. In this case, $Q_V$-value is assumed to be uniform through a sample due to only small variation of temperature.
- by integrating a heat removed by helium during and after a burp until temperature returns to an equilibrium value, and subtracting thermal power induced by neutrons (4.5-5.2 Watts). In this case, $Q_V$-value is actually averaged over a sample.
- for segmented samples, $Q_V$-value near a place of the central thermocouple can be estimated directly knowing its records before and after a burp, $T_{ign}$ and $T_{max}$:

$$Q_V = [H_{sample}(T_{max}) - H_{sample}(T_{ign})],$$

where $H$ is heat content in sample material at given temperature $T$.
- By computer simulation of nonstationary heat diffusivity process, it was possible also to calculate $Q_V$-value by making several iterations of $Q_V(t)$ until heat transfer power (experimental, time-dependent value) coming into the copper walls of the capsule is equal to the calculated heat transfer power going out of a sample:

$$c_{Cu}(T_{Cu}) \cdot \frac{dT_{Cu}}{dt} \cdot m_{Cu} + \lambda_{sample} \cdot \frac{dT_{sample}}{dt} \cdot S_{sample} = 0,$$

where $S_{sample}$ is an area of a boundary surface between a sample and the copper walls of the capsule, and $c_{Cu}$ is a specific heat of copper.

This procedure enables one also to estimate duration of energy release in a burp and distribution of energy release in time (though, quite roughly) as well.

6. RESULTS AND ANALYSIS OF SOLID METHANE EXPERIMENTS

6.1. Stored energy and Saturated curves

Let us call a concentration of radicals (or: «stored energy», which is identical), versus irradiation time by a ‘saturation curve’, and a saturated amount of stored energy - by ‘saturated stored energy’, $Q_\infty$. Relation between molar concentration of radicals $n$ and stored energy $Q, J/g$, is: $Q = n \cdot 1.08E+4$, if radicals are CH$_3$, and $Q = n \cdot 1.35E+4$, if radicals are H, see Appendix.

Amount of stored energy was estimated by methods described above. All methods are based on estimation of a magnitude of energy released during a burp which appeared to be not strictly reproducible. That is why a reconstruction of an exact saturation curve was impossible.
Estimated values of energy released in burps, are given in Table 3 and in Fig. 4. It is interesting to mention that in one case (experiment #1) a burp proceeded in two stages, see a relevant figure in the Appendix.

Taking for granted that only one type of radicals is responsible for burping, we conclude that kinetics of saturation of radicals must be described by an equation

\[ \frac{\partial n}{\partial t} = R(t) - D^* K_1(T) n - K_2(T) n^2 \]

where \( n \) is a space averaged concentration of radicals, mol/mol, \( R(t) \) is radical production rate (in the case of methane, it is time dependent as was discovered during IBR-2 solid methane moderator investigation), \( D^* \) is an absorbed dose rate (in other word, radiation load), and \( K_i(T) \) are recombination reaction rate coefficients. The second order term describes recombinations due to diffusion of radicals, and \( K_2(T) \) is assumed to have an Arrhenius form:

\[ K_2(T) = K_{20} \exp\left(-\frac{T_{\text{act}}}{T}\right) \]

where \( T_{\text{act}} \) is the so called "activation energy" expressed in degrees Kelvin. But the term of first order describes recombinations induced by hot tracks of recoil protons, and \( K_1(T) \) is a function of temperature of a form which is different from an Arrhenius form. It is evident that it has to be a function smoother than \( K_2(T) \), and can hardly be restored theoretically in an explicit form. The simplest consideration (see [9], formula (6)) showed that approximation of \( K_1(T) \) with an Arrhenius form gives \( T_{\text{eff},\text{act}} = T_{\text{act}} \left(T/T_{\text{tr}}\right)^2 \), where \( T_{\text{tr}} \) is some effective temperature characterizing recombination of radicals around a hot track.

By comparing experimental data on burps of different solid methane moderators (IPNS, KENS, IBR-2) and of the current results, it is possible to notice that values of saturated energy are almost the same for all cases. It only can be so if the term of the second order of \( n \) in Eq. 1 is negligibly small in comparison to the first order term in the phase of building up
of radicals, that is, before a burp. Otherwise, saturated concentration of radicals would sharply depend on irradiation temperature as \( T_{\text{act}} \gg T_{\text{eff, act}} \), which was not actually observed.

For analyzing experimental data, we applied Eq. #1 without the second order term. Assuming primarily that radical production rate is time independent, we have for an amount of stored energy (SE) in the course of irradiation:

\[
Q_{\text{act}}(t) = \frac{1}{K_1(T)} \cdot (1 - \exp(-t/\tau)) = Q_\infty \cdot (1 - \exp(-t/\tau))
\]  

(2),

where \( \tau = (R K_1)^{-1} \) is a “saturation time”.

Table 3. Estimated values of an energy released in a burp, solid methane samples

<table>
<thead>
<tr>
<th>N° of experiment</th>
<th>2.14</th>
<th>2</th>
<th>3b</th>
<th>5</th>
<th>7</th>
<th>11</th>
<th>13</th>
<th>14</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q, J/g</td>
<td>80</td>
<td>~50</td>
<td>~50</td>
<td>~45 for 25.5K</td>
<td>120-180</td>
<td>45-50 for 26 K</td>
<td>38</td>
<td>~60</td>
<td>~50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>N° of experiment</th>
<th>18</th>
<th>19</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>47</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q, J/g</td>
<td>72-100</td>
<td>95-100</td>
<td>46-56</td>
<td>33-37</td>
<td>~65°(25.5K)</td>
<td>~100°(18K)</td>
<td>~100</td>
</tr>
</tbody>
</table>

Notes: *)- For segments of big sizes the Q-value is space-dependent

Basing on a host of experimental data on \( Q_{\text{act}}(t) \), see in Table 3 and Fig. 4, and on Eq. 2, \( Q_\infty, R \) (we assume that \( R \) now represents «energy storing rate», J/g/h, which proportional to radical production rate), and \( \tau \)-value were deduced. Saturated stored energy, \( Q_\infty \), can be estimated with an appropriate precision only for temperature range 21-26K. Its temperature dependence can be described with a linear equation with an error about \( \pm 10% \): |

\[
Q_\infty, J/g \approx 13 \cdot (30 - T_{irr})
\]

(2a).

Then we have received

\[
R \approx (13 \pm 1) \text{ J/g/hour},
\]

which is equivalent to a maximal rate of energy accumulation in solid methane \((1.6 \pm 0.2) \%\) of an absorbed dose. The \( \tau \)-value can be described, naturally, also with a linear function is within 20% accuracy:

\[
\tau, \text{ hours} \approx 1.0 \cdot (30 - T_{irr})
\]

(2b).

Approximation of \( Q_\infty \) and \( \tau \)-values in the Arrhenius form is worse than in linear one; in this case, \( T_{\text{eff, act}} \) varies with temperature from 100 K at 26 K down to 70 K at \( T<21K \). Formally, one can apply relations (2a) and (2b) for irradiation temperatures 18-21 K also: a radical saturation curve calculated with such defined \( Q_\infty \) and \( \tau \)-values for irradiation time \(< 12 \text{ hours} \) wouldn’t contradict with experimental data, but prediction beyond this time limit is quite unreliable. We can judge from experiment #7 that at temperature \(< 13-14K \) (phase III of solid
methane) an energy storing rate \( R \) is as high as \( R \approx 20-30 \text{ J/g/hour} \), which is equivalent to a maximal rate of energy accumulation in solid methane (2.5\%÷4.2\%) of an absorbed dose.

Second approximation to an estimation of an amount of stored energy (SE) in the course of irradiation was made assuming radical production rate \( R(t) \) be time dependent due to building up of scavengers of radicals (ethylene et al.). In [17] it is shown that \( R(t) \) decreases with irradiation time following a law:

\[
R(t) \approx 0.5 R_0 \left( 1 + \exp\left(-\frac{D}{\alpha t} - \frac{D_0}{D_0} \right) \right) = 0.5 R_0 \left( 1 + \exp\left(-\alpha t \right) \right)
\]  

(3)

where \( D_0 \approx 8900 \text{ J/g ± 20 \%} \), \( R_0 \) is radical production rate at a start of irradiation, equal to 1.6 ± 0.2 \% of absorbed dose rate, and \( \alpha = (0.007 \pm 20\%) \cdot R_0 \), accordingly. Dimension of \( \alpha \) is \( h^{-1} \), and of \( R - \text{J/g/h} \). It follows from analysis of Eq.1 that solution with time dependence of \( R \) has maximum of concentration of radicals (or stored energy) before reaching saturation. The higher is \( K_1 \), that is, temperature of irradiation, then the higher is maximum relative to saturated value of \( Q \). This effect is more distinct with increasing of dose rate. It explains in most part a discrepancy between \( T_{\text{eff,act}} \) estimated in URAM-1 experiments [6] where it was equal to 140 ± 15 K, and the URAM-2 experiments (70÷100K): dose rate at URAM-2 was about twice of that for URAM-1. Also, it explains an unexpectedly low value of stored energy in long term irradiation experiment # 21 at T=23-24K, see hollow triangle in Fig 6. It is best to satisfy experimental values of \( Q(t) \) , with taking in mind time dependence of \( R \) by (3) and by taking function \( K(T) \) equal to:

\[
K(T) \approx 1.3 \left( -\frac{120 \pm 10}{T} \right), \text{ dimension of } K \text{ is g/J}
\]  

(3a)

Now, \( T_{\text{eff,act}} = (120\pm10) \text{ K} \) agrees with activation temperature estimated in URAM-1 experiments within error limits. One should take in mind that \( Q_{\text{crit}} \), calculated from Eq.1 with time dependence of \( R \), is equal to 1/2\( K_1 \) instead of 1/\( K_1 \). With such defined \( K(T) \), maximum of \( Q(t) \) follows approximately to Arrhenius law with \( T_{\text{eff,act}} = (90÷100)K \); at T=26K \( Q_{\text{max}} = 50 \text{J/g} \), at T=21K \( Q_{\text{max}} = 120 \text{J/g} \). Amounts of saturated energy \( Q_{\text{1inf}} \) defined by (2a) relation, \( Q_{\text{max}} \), and \( Q_{\text{2inf}} \) defined by Eq.1 with \( K(T) \) by the relation (3a), are displayed in Fig 5.

**Figure 5.** Stored energy in methane versus irradiation temperature:

- \( Q_{\text{1inf}} \) – saturated energy, evaluated from URAM-2 experimental data;
- \( Q_{\text{2inf}} \) – the same, evaluated with time dependence of radical production rate;
- \( Q_{\text{crit}} \) – evaluated critical values of \( Q \);
- \( Q_{\text{max}} \) – maximal value of \( Q \), evaluated from URAM-2 experimental data

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6.2 Condition for thermally stimulated burps

Regularities which were perceived for condition of thermally stimulated burps are as follows:

- a burp could always be induced by temperature rise of cooling helium if energy accumulated in a sample exceeded 35-40 J/g (more than 3 hours of irradiation) and size of sample is $\geq 0.3$ mm.

- stored energy before a burp is close to linear to a temperature difference between temperature of ignition and some definite temperature $T_{cl}$, see Fig. 6. In the figure, data on some big samples of a segment type (because of the uncertainty of ignition temperature values in the case) are not presented. Two points (both 120 J/g and 180 J/g) present experiment #7 in view of impossibility to choose between two methods of restoration of the $Q_{se}$-value. It is believed (and this is clear in experiments with water ice, see a relevant section of the report) that equations of line

$$Q_{se} = C \cdot (T_{cl} - T_{ign})$$

(4)

can’t be absolutely identical for different temperature of irradiation. But, because of low statistics of experiments, we could derive for the case one averaged curve based on a host of experimental runs. For the curve, $T_{cl}$ is equal to 35-36K which is consistent with the temperature of the threshold of mobility of radicals [13]. The factor $C \approx 10$ J/g/K.

![Figure 6. Critical and maximal quantities of stored energy in solid methane.](image)

- almost no dependence of a size of a sample on ignition condition; only the smallest samples ($\leq 1.0$ mm) need slightly higher temperature for ignition of a burp at identical condition of irradiation.

6.3 Pulse shape and duration of burps

Duration of burps and their temporal structure was deduced from computer processing of experimental readings of the thermocouples fastened to the copper wall of the sample capsule. As duration of burps were always much shorter than characteristic time of helium cooling, a process of heat transfer from a sample to the copper wall is acceptable to be considered
as adiabatic one. Then, solution of a non-stationary, heat diffusion equation by inspection enables one to estimate specific heat production rate versus time in the vicinity of the wall and in the region near the thermocouple inside the capsule as well.

Some regularities were discovered:
- steep rise of temperature begins at once in each point of a sample regardless of a size of a sample, over a time interval of 0÷0.4 sec.
- time structure of a burp is close to the non-symmetric Gaussian, with back front shorter.
- effective duration of a burp varied from ≤ 0.2s (0.2 sec is an experimental limit of time resolution) up to ~1s according to stored energy at a given point of a sample; Q-dependence of burp duration was hard to estimate; it looks to be closer to the second power of 1/Q.

Typical result of reconstruction of time dependence of recombination power in the burp #11 is in Fig. 7.

![Figure 7. Pulse shape of the burp # 11.](image)

7. WATER ICE

7.1 Stored energy and Saturated curves

An amount of stored energy was estimated by different methods described above. Results are in Table 4 where Q-values evaluated from temperature response of a thermocouple placed inside the sample chamber, are placed in the second row, \( Q_{12} \), and in the third row Q-values evaluated by balancing heat removed by helium are given (the last method was available only for spontaneous burps).
Table 4. Estimated values of an energy released in a burp, water ice samples

<table>
<thead>
<tr>
<th>No of an experiment</th>
<th>24</th>
<th>25</th>
<th>26</th>
<th>27</th>
<th>28</th>
<th>29</th>
<th>30</th>
<th>31</th>
<th>32</th>
<th>33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q_{22}, J/g</td>
<td>100</td>
<td>138</td>
<td>110</td>
<td>65</td>
<td>108</td>
<td>115</td>
<td>148</td>
<td>148</td>
<td>70</td>
<td>68</td>
</tr>
<tr>
<td>Q_{He}</td>
<td>125</td>
<td>162</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No of an experiment</th>
<th>35</th>
<th>36</th>
<th>37</th>
<th>38</th>
<th>41</th>
<th>42</th>
<th>43</th>
<th>52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q, J/g</td>
<td>146</td>
<td>144</td>
<td>143</td>
<td>62.6</td>
<td>145</td>
<td>100</td>
<td>70</td>
<td>54</td>
</tr>
<tr>
<td>Q_{He}</td>
<td>170</td>
<td>149</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No of an experiment</th>
<th>2.5 (1)</th>
<th>2.5 (2)</th>
<th>2.5 (3)</th>
<th>2.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q, J/g</td>
<td>95</td>
<td>108</td>
<td>100</td>
<td>280</td>
</tr>
<tr>
<td>Q_{He}</td>
<td>34</td>
<td>43</td>
<td>37</td>
<td>-</td>
</tr>
</tbody>
</table>

For analyzing experimental data, we applied again Eq. #1 without dependence R(t), and derived R, τ and Q_{∞} values. The τ-value («saturation time») and saturated stored energy Q_{∞} appeared to be near linear to irradiation temperature as for solid methane:

\[ \tau \approx 0.6 (50 - T_{irr}) \]

\[ Q_{\infty} \approx 12 (50 - T_{irr}) \]  \hfill (5)

Q_{∞}-value may be defined by Eq. (5) for irradiation temperature > 36 ÷ 37 K only. At lower temperature, saturation of stored energy can’t be reached because a spontaneous burp occurs before saturation – at 100 ÷ 148 J/g. Experimental errors of τ-value is within ± 20%. As it follows of Eq. 1, radical production rate value (or «energy storing rate») R = Q_{∞}/τ. For T_{irr} ≈ 20 K R-value was estimated directly from experiments with short irradiation time. Then, we have

\[ R \approx 20 ± 24 \text{ J/g/h} \]

which is almost independent on irradiation temperature and is equivalent to a maximal rate of energy accumulation as high as 5.4% ± 0.4% of absorbed dose rate. Values of Q_{∞} in ice at T > 35K, deduced from URAM-2 experiments are in agreement with previously calculated (see Fig. 2 in [11]) if one takes into account that 1% of concentration of radicals corresponds to 138 J/g of stored energy.

Results given above are true for bulky samples of ice. It was observed that radical production rate, or «energy storing rate», (and saturated stored energy accordingly) depends on methods of ice preparation. If ice samples (5 mm beads) are prepared by freezing water droplets in liquid nitrogen, then energy storing rate is \( 2.5 ± 3 \text{ factor less} \) than that of ice prepared by slow freezing. This phenomenon was referenced earlier [12].

7.2 Degradation of thermal conductivity in the course of irradiation.

Earlier unknown effect in ice (and hydrates also) under fast neutron radiation was discovered, namely: thermal resistance of ice increases with irradiation time. Temperature difference of two distanced thermocouples in ice changed from almost zero at the start of irradiation (thermal conductivity of ice are very high at low temperature [13] - 40 W/m/K at 20 K) up to
Saturation curve of thermal resistance goes close to that of radicals. It seems that radicals may be responsible for the effect absorbing phonons. Thermal conductivity of ice at saturation is close to that of solid methane, only 50% higher. This phenomenon can be useful for experimental study of radiation effects in ice.

Figure 8. Comparison of saturation of inverse thermal conductivity of ice value (left scale) and stored energy (right scale).

7.3. Condition for spontaneous and thermally stimulated burps

Regularities which were perceived for condition of burps are as follow:

- A burp could always be induced by temperature rise of cooling helium if energy accumulated in a sample exceeded 30-40 J/g (as low as for solid methane).
- In opposite to methane, for stimulated burps in ice no evident universal relation between stored energy and temperature of ignition was found. Nevertheless, for each of eleven induced burps, the same equation of line as for methane fits experimental data more or less (see Fig. 9):

\[ Q \approx C \cdot (T_{cl} - T_{ign}) \]  

But now, \( T_{cl} \) is not identical for different temperature of irradiation and is equal approximately to

\[ T_{cl} \approx 1.5 \ T_{irr} + 6. \]  

Factor \( C \approx 7-8 \ J/g/K \), being weakly dependent on \( T_{irr} \), is close to that of methane.

- No (or only small) dependence of a size of a sample on ignition condition was observed for the range of effective sizes 15-5 mm;
Nine spontaneous burps were observed in body ice samples, four of which occurred when $>145\text{ - }148 \text{ J/g}$ was stored. Five burps occurred at lower $Q$ (100 and 138 J/g). Ice samples displayed no burps at $T_{irr} > 34 - 35 \text{ K}$.

Beads of ice in argon matrix displayed no spontaneous burp at irradiation time <13 h.

Figure 9. Quantities of stored energy in water ice samples.

7.4. Pulse shape and duration of burps

Duration of burps appeared to be dependent on a released energy in a way similar to that for solid methane. In the range of $Q \approx 60\text{ - }150 \text{ J/g}$ it varied from 2 to 0.5 sec.

8. TETRAHYDROFURANE (THF) AND METHANE HYDRATES

8.1 Stored energy and Saturated curve

Both hydrates studied, and beads of ice in argon also, displayed similar regularities in saturation curves of radicals (or «stored energy»), see in Table 5 and Fig.14. Energy storing rates in beads of ice and in methane hydrate beads (which were of 2-4 mm size) are identical - 8 - 9 J/g/h; for THF hydrate it looks to be slightly higher - about 10 J/g/h. In any case, these values are 2.5-3 times less than energy storing rate in body samples of ice. These facts allow to suppose that hydrates behave like ice with defects (or amorphous ice), in the sense of kinetics of radicals. This conjecture is consistent with well known facts of general similarity of physical properties of hydrates.

Table 5. Estimated values of an energy released in a burp, hydrates (tetrahydrofuran and methane)

<table>
<thead>
<tr>
<th>No of experiment</th>
<th>39</th>
<th>40</th>
<th>44</th>
<th>45</th>
<th>49</th>
<th>50</th>
<th>51</th>
<th>53</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$, J/g</td>
<td>38</td>
<td>115</td>
<td>100</td>
<td>55</td>
<td>38</td>
<td>&gt; 70</td>
<td>78</td>
<td>80-110</td>
</tr>
<tr>
<td>$Q_{He}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>87</td>
</tr>
</tbody>
</table>
Due to insufficient number of irradiation runs with hydrates, it is impossible to restore data on saturation time. One only may conclude that it is somewhere around 10-15 hours at irradiation temperature 25-30 K, that is, close to that of pure water ice.

![Figure 10](image-url) Stored energy versus irradiation time for hydrates and beads of ice

8.2. Condition for spontaneous and thermally stimulated burps

From four experiments with THF hydrates (see in Tables 2 and 5) it can be deduced that this substance behaves similar to pure ice. Duration of burps in THF appeared to be longer than in pure water ice due to slow leading front, see in relevant figures in Appendix. One spontaneous burp occurred in THF hydrate after irradiation for 13 h at temperature 20÷27 K with $Q=100$ J/g (experiment # 44). Another, longer irradiation at the same temperature (experiment #40) displayed but induced burp with $Q=115$ J/g.

Similar behavior is displayed by methane hydrate. One spontaneous burp occurred at irradiation temperature 20÷25 K after 13 h with $Q \sim 80÷90$ J/g (experiment #50). At irradiation temperature $>25$ K no spontaneous burp was registered even for longer time of irradiation (experiments #51, 53), see in Table 2a and 5 and plots of burps.

As distinct from pure water ice when both spontaneous and induced burps were equally fast (or no burp occurred), induced burps in hydrates had a long leading front.

Finally, one may conclude that spontaneous burps occur in hydrates of THF and methane at irradiation temperature around 20 K and stored energy $\geq 80-100$ J/g, absorbed dose $>5.1$ MGy, accordingly. Temperature limit of spontaneous burping is near to 25K. Total combination of experimental data on ice and hydrates samples points to an existence of effect of «amorphous» state of ice (hydrates can be considered also as pure ice with defects) on both production of stabilized radicals and their critical concentration.
APPENDIX

Some useful relations and values:

1. Bound energy of radicals:

<table>
<thead>
<tr>
<th>Radical</th>
<th>Energy (kcal/mol)</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃+CH₃</td>
<td>- 83</td>
<td>3.6</td>
</tr>
<tr>
<td>H+CH₃</td>
<td>- 101</td>
<td>4.38</td>
</tr>
<tr>
<td>H+OH</td>
<td>- 117.5</td>
<td>5.095</td>
</tr>
<tr>
<td>H+H</td>
<td>- 103.2</td>
<td>4.476</td>
</tr>
<tr>
<td>H+OOH</td>
<td>- 90</td>
<td>3.9</td>
</tr>
<tr>
<td>HO+CH₃</td>
<td>- 90</td>
<td>3.9</td>
</tr>
<tr>
<td>OH+OH</td>
<td>- 51</td>
<td>2.21</td>
</tr>
</tbody>
</table>

2. Relations between concentration of radicals n, mol/mol, and stored energy Q, J/g:

\[ Q = n C \times 10^4; \]
- \( C = 1.08 \) if radicals are \( \text{CH}_3 + \text{CH}_3 \),
- \( C = 1.35 \) if radicals are \( \text{H} + \text{H} \) in methane,
- \( C = 1.18 \) if radicals are \( \text{CH}_3 + \text{H} \),
- \( C = 1.37 \) if radicals are \( \text{H} + \text{OH} \),
- \( C = 1.20 \) if radicals are \( \text{H} + \text{H} \) in water.

3. Absorbed dose rates:

<table>
<thead>
<tr>
<th>Region</th>
<th>Material</th>
<th>Dose Rate (W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>in the URAM-2:</td>
<td>methane</td>
<td>0.22</td>
</tr>
<tr>
<td>water</td>
<td>–</td>
<td>0.11</td>
</tr>
<tr>
<td>in the ESS:</td>
<td>methane</td>
<td>2</td>
</tr>
</tbody>
</table>

CONCLUSION

Notwithstanding fair amount of experimental data on spontaneous burps, it is still impossible to derive well balanced theory of this phenomenon. Discussion on the subject and analysis of spontaneous burps possibility in ESS moderator is in the relevant presentation to this AcoM 6 Meeting.

REFERENCES

2. «URAM-2: Irradiation facility & the project on study on radiation effects in cold moderator materials». Poster presentation at the ESS General Meeting in Seggau, Austria, 26-29 September 2001
APPENDIX. Graphs of burps.
The JESSICA Experiment – Part I: Improvements of the JESSICA-Experiment

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A. Smirnov
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ABSTRACT

In this article we like to report on the progress of the JESSICA experiment. The experimental setup will be described and the experimental method will be presented. Proton beam monitoring and results from water and polyethylene will also be mentioned. The results from the cold moderator experiments are described in another report on JESSICA [1] held on this meeting. In the end we give an outlook to the upcoming experiments with further cold moderator materials.

1. INTRODUCTION

JESSICA (Jülich Experimental Spallation Target Set-up In COSY Area) is an experiment carried out at the Jülich proton accelerator COSY. The aim is to investigate the neutronic behavior of advanced cold moderator materials in a realistic environment. On this a target-moderator-reflector assembly was constructed based on the reference design of the ESS [2] from 1996. The target containing 35 l of mercury is located in the center of the lead reflector. The surrounding reflector has a diameter of 1.3 m and a height of 1.3 m. The moderators are placed in the so called wing geometry. This means two moderators are mounted above and below the target to prevent fast neutrons from the target directly leaking out of the system. This reduces the fast neutron background considerably. Whereas three moderators are filled with water the lower upstream moderator position is used to study various cold moderator materials. However the aim of JESSICA is twofold: On the one hand the experimental investigation of the neutronic behavior of advanced cold moderators is the main topic of the experiment. On the other hand Monte-Carlo simulation codes can be validated as well. Especially new neutron scattering kernels can be validated and checked against measured data.

During the start-up phase of the experiment we measured water and polyethylene because of their well known spectra. The advantage of polyethylene was the possibility to check the sensitivity of the experiment to different moderator configurations like de-coupling and de-coupling/poisoning. The first cold moderator experiments were carried out with ice at 20 K and 70 K and during the last beam time we measured the first time the spectra of a methane-hydrate moderator.
2. EXPERIMENTAL SETUP

Fig. 1 will give an impression of the experimental setup. The both proton monitors ICT (Integrating Current Transformer) [3] and WCM (Wall Current Monitor) [4] are located in the proton beam line in front of the target. Whereas the ICT measures the current induced by the magnetic field of the proton beam in a coil surrounding the proton beam line, the WCM measures the mirror current in the metallic beam tube. With these two proton monitors we obtain the number of protons per pulse. This data are import for normalization of the neutron time-of-flight, respectively the derived energy spectra, and the comparison of absolute values with Monte-Carlo simulations. Between the end of the proton beam line and reflector a plastic scintillator is mounted, generating a start signal for the data acquisition system when a proton pulse passes the scintillator.

For our experiments we use the moderator in the so called bottom up-stream position, this means the moderator is placed below the target in the most brilliant position. In case of the time-of-flight measurements the moderator is oriented under 45° to the proton beam axis. As a neutron detector we are using a LiGdBO-Detector [5,6]. The neutron flight path has a length of 5.37 m (from moderator surface to detector surface). In order to reduce background effects the neutron flight path as well the detectors are surrounded with polyethylene to moderate fast neutrons. The neutron neutron beam tube itself is constructed as a double wall tube. The space between outer and inner tube is filled with boron acid to absorb thermal neutrons.

![Figure 1. Setup of the JESSICA experiment. The drawing shows the proton monitor, start counter, neutron detectors, moderator, and the graphite crystal. Dimensions of the flight path are in mm.](image)

In case of the measurements of the time structure of specific wavelengths, selecting via bragg reflection at a graphite crystal, we have the possibility to use a time focusing assembly in order to achieve a better time resolution [7,8]. Here the moderator surface, the crystal surface, and the detector surface are aligned parallel. Whereas the experiments with water and ice were carried out with a non-time focusing assembly, it was the first time we used the time focusing assembly when studying the methane-hydrate moderator.
3. PROTON BEAM MONITORING

To normalize the data and comparison with Monte-Carlo simulation the determination of the number of protons per pulse is dispensable. Even for the on-line data analysis these data are important to check if the experiment is running correctly. Fig. 2 shows the correlation of the both proton monitors. As expected the proton monitors show a linear correlation. Further can be seen, that the ICT measures a 30 % lower proton beam intensity than the WCM.

![Figure 2](image1.png)

**Figure 2.** Correlation between both proton monitors (ICT and WCM).

With the pulse-wise data we are able to look on further correlations, available online and off-line, to check the experiment. In Fig. 3 the correlation between ICT and neutron detector is plotted. Here also a linear correlation can be seen, as expected. Fig. 2 and also Fig. 3 illustrates, that the intensity of the proton beam impinging on the target varies from pulse to pulse. But the ratio between neutrons and protons has to be constant, because the n/p-ratio depends only on the incident proton energy, material of target, moderator, and reflector, and geometry.

![Figure 3](image2.png)

**Figure 3.** The left picture illustrates the correlation between ICT and the neutron detector. The right picture shows the distribution of the neutron to proton ratio (n/p-ratio).
All these parameters are kept constant during the experiment. The distribution of the n/p-ratio is also plotted in Fig 3. You can see that these ratio is nearly constant.

3. RESULTS FROM WATER AND POLYETHYLENE

We started our experiments with a water moderator at ambient temperature. The advantage of such a moderator is the well known spectra which is helpful to test a new experiment. The measurement of the thermal neutron time of flight spectrum was performed in two steps. The first measurement counts all neutrons leaving the moderator including background. To eliminate the background a further measurement is performed. In this second measurement only those neutrons are detected, which are not absorbed in an additionally inserted cadmium layer in front of the neutron flight path. The high neutron absorption cross section of cadmium for thermal neutrons prevents them to reach the detector. The difference of both spectra results in the time of flight spectra for the thermal neutrons. Thus these spectra are normalized to the number of incident protons they can directly compared with Monte-Carlo simulations. In Fig.4 the time of flight spectrum from a water moderator is shown as well the results from a MCNPX [9] simulation. The detector efficiency is included in the simulations.

Unfortunately both curves do not match very well. The difference between experimental data and simulated ones is about 60%. Possible reasons for that could be manifold. One possibility is the assumption of a higher detector efficiency in the simulation than the detector really has due to an inhomogeneous detector material. This would lead to an overestimation of the resulting curve. A further reason could be dead-time effects in the measured spectra reducing the real intensity. The last point is an error in the measurement of the absolute value of the number of proton per pulse. Nevertheless the shapes of both curves argue very well. This can be seen when normalizing the data to one at the maximum.

After we saw that the measurement of the time-of-flight spectra works, we started measurements on the time structure of the neutrons to obtain more information about the thermalization in the moderator. Beneath the water moderator we tested a polyethylene moderator because the moderator configuration can be changed easily. We investigated a coupled, decoupled and a decoupled/poisoned moderator configuration. Decoupling and poisoning was
performed with 1 mm layers of cadmium. The aim was to demonstrate the sensitivity of the experiment to changes influencing the pulse width of the neutron pulses. Figure 5 shows the measured Bragg reflexes for $\lambda = 4.74\text{Å}$, $\lambda/2 = 2.37\text{Å}$, $\lambda/3 = 1.57\text{Å}$, $\lambda/4 = 1.19\text{Å}$ and $\lambda/5 = 0.95\text{Å}$ for a coupled and de-coupled/poisoned polyethylene moderator. It can be seen that the pulse widths as well as the peak intensities are decreasing by de-coupling and poisoning the moderator. The time resolution of the experiment is 1 µs, but in Fig. 5 the data are compressed by a factor of 10 to obtain better statistics resulting in a time resolution of 10 µs.

Figure 5. Bragg reflections of neutron pulses for a coupled (solid line) and a de-coupled/poisoned (shaded area) polyethylene moderator.

In Fig. 6 we compare the pulse widths for the above mentioned wavelengths for a coupled and a de-coupled/poisoned polyethylene moderator. This plot illustrates the decrease of the pulse width when de-coupling and poisoning the moderator.

Figure 6. Pulse width as FWHM versus wavelength $\lambda$ for a coupled (triangle symbols) and de-coupled/poisoned (circle symbols) polyethylene moderator measured at JESSICA.
4. CONCLUSIONS

We demonstrated that the JESSICA experiment finished its start-up phase successfully and is now able to start measurements of advanced cold moderator materials in a realistic target-moderator-reflector assembly. Measurements with water at room temperature and different configurations of a polyethylene moderator showed the expected results. We started cold moderator experiments with an ice moderator at 20 K and 70 K. For the first time we investigated a cold moderator based on methane-hydrate. These results are presented in a further report on this meeting [1].

In future we like to measure a solid methane moderator to complete the study of a methane-hydrate moderator. As a reference moderator we will measure a hydrogen moderator, because it is one of the standard cold moderators used at several neutron sources around the world. A more ambitious aim of our experiment is the measurement of a methane pellet moderator to demonstrate its feasibility. As result of the discussions during this meeting we included a mesitylene moderator in our experimental program.

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[3] Bergoz
A Cryogenic Moderator System for JESSICA, a Test Facility for Advanced Cold Moderators

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ABSTRACT

In this article we like to report on building up and running a cryogenic moderator system for JESSICA, a full scale model of the target-reflector-moderator system for the European Spallation Source (ESS). The cryogenic moderator system can be charged with different fluids, solids and pellets in fluids at cryogenic temperatures.

1. INTRODUCTION

Common cold sources for neutron research experiments are operated with cold hydrogen moderators. However, a study by Inoue et al. [1] shows that e.g. solid methane yields 3 to 4 times more low-energy neutrons than conventional sources with liquid hydrogen at the same temperature of about 20 K (Fig. 1). The problems of operating the moderator system with a solid methane block are its very low thermal conductivity at low temperatures (removal of deposited energy), the spontaneous exothermal recombination of radiolysis products (H+, CH3-) that can easily destroy the moderator vessel, and the deterioration of the slowing-down properties of methane (formation of higher alkane homologues) due to radiation damage.

Figure 1: Neutron beam intensity and neutron energy of different moderator materials [1]
JESSICA (Juelich Experimental Spallation Target Set-up In COSY Area) has been built up at the COSY proton accelerator in Juelich to investigate the neutronic performances of advanced cold moderators in a realistic environment [2]. The JESSICA experiment is performed in the framework of an international collaboration among 12 neutron research laboratories:

- ANL, Argonne National Laboratory, USA,
- FZJ, Forschungszentrum Jülich GmbH, Germany
- JAERI, Japan Atomic Energy Research Institute, Centre for Neutron Science, Japan,
- JINR, Joint Institute for Nuclear Research, Russia,
- KEK, High Energy Accelerator Research Organisation, Japan,
- LANL, Los Alamos National Laboratory, USA,
- ORNL, Oak Ridge National Laboratory, USA,
- PSI, Paul Scherrer Institut, Switzerland,
- RAL, Rutherford Appleton Laboratory, UK,
- SOREQ, Israel,
- Technical University Graz, Austria,
- University of Hokkaido, Japan.

This international collaboration was formed to study science and engineering aspects of high-power pulsed neutron spallation targets, namely the neutron intensity and pulse shape optimization upon varying the target and reflector material, geometry, moderators and proton beam energy [3].

2. JESSICA ASSEMBLY

The reflector is a stainless steel construction, completely filled with lead rods except of the positions for the target, the proton beam line, the neutron beam lines and the moderators. Figure 2 is an overview of the JESSICA hall where the proton beam line coming from the COSY proton accelerator onto the target (pipeline in the background including WCM and ICT) can be seen. The pipeline going to the left side on Fig. 2 is the neutron beam line including neutron measurement facilities.

Figure 2: View into the JESSICA hall. WCM: Wall Current Monitor. ICT: Integrating Current Transformer in the proton beam line.
During beam time the target which is positioned on a trolley has to be moved into the reflector horizontally. To receive neutrons out of the proton beam coming from COSY the target is filled with 35 dm³ (liters) of mercury.

Above and below the target the reflector has recesses for two moderators above the target and two moderators below the target. Both moderators above the target and one of the moderators below the target are water moderators at room temperature. A machine-cooled cryogenic moderator with temperatures below 10 K can be positioned below the target.

3. CRYOGENIC MODERATOR SYSTEM

The moderator materials to be tested are namely water, solid methane as a block (CH₄) and in form of pellets, liquid hydrogen (H₂), methane hydrate (clathrate) and a combination of either methane pellets in liquid hydrogen or methane hydrate in liquid hydrogen. Thus the design of the cryogenic system has to allow very different materials to be used in the moderator vessel. It has to be suitable to put e.g. water into the moderator vessel at ambient temperature and to put in e.g. methane hydrate at cold temperatures as liquid nitrogen temperature (77 K). Furthermore it has to allow the condensation of a gas such as hydrogen from a storage container into the moderator vessel at temperatures below 20 K. Additionally, a technical solution has to be found which avoids the formation of explosive gas mixtures when using methane or hydrogen as moderator materials.

Figure 3: Design of the moderator on the cold head including surrounding vacuum chambers and double lid system
The moderator system consists of the moderator vessel on a cold head, insulated by two vacuum chambers surrounding the moderator vessel (see Fig. 3). Other main components are two storage containers for the gas to be condensed in the moderator vessel, a vacuum pumping system with three vacuum pump stations, each including a roughing pump and a high-vacuum pump to evacuate the storage containers or the vacuum chambers or the moderator vessel.

There are two possibilities to fill the moderator vessel with moderator material: if the moderator material is liquid or solid at ambient temperature it can be filled into the vessel through a double lid system (Fig. 3); if the moderator material is gaseous at room temperature the moderator vessel will be filled by condensing the gas into the vessel. For this purpose a piping system including gas storage containers has been installed.

The moderator vessel is being cooled by a cold head in conjunction with a compressor unit to generate cryogenic temperatures. Temperatures down to 10 K are achieved with this double-stage cold head.

Two tubes had been built for gases to be condensed into the moderator vessel. One of the tubes is twisted around the first refrigeration stage with about 80 K to precool the gases to be condensed in the moderator vessel (Fig. 4). The other tube is surrounded by a heater for gases to be condensed which have a boiling point above 80 K. Methane would even become solid at the 80 K refrigerator stage and the tube twisted around the first refrigeration stage would be blocked without additional heating.

Figure 4: Moderator vessel M on the cold head. The first stage of the cold head C delivers about 80 K, the second one 8 K. B: Bottom flange to fix the cylinders for the vacuum chambers. S: warm gear spindles for elevating the moderator head to the final position close to the target.
The moderator vessel including its vacuum chambers and the cold head are installed on a small lifting platform. This platform can be moved vertically by a lifting device. Thus the moderator vessel can be positioned vertically directly below the target. The lifting platform including its lifting device driving system, the three high vacuum pumps and several valves and measuring instruments are fixed on a trolley (Fig. 5). The trolley can horizontally be moved between the reflector and a glove box. The glove box with a helium atmosphere inside is beside the target-reflector-assembly (Fig. 2, right). At the bottom of the glove box the moderator vessel can be connected and the double lid system can be opened (Fig. 3). So it is possible to fill methane pellets or methane hydrate under He-atmosphere into the moderator vessel at liquid nitrogen temperatures without getting any water or ice or oxygen respectively, into the moderator system.

**Figure 5**: Vacuum housing (V) of the moderator comprising insulation, cold head, lifting platform (L), vacuum pumps (P) and valves (v) on the trolley

JESSICA is operated in a nuclear control zone. Thus, volatile gases like methane and hydrogen have to be monitored while venting to the atmosphere. Because the monitoring system is not explosion resistant, the following precaution has been implemented at JESSICA: by checking the concentration of hydrogen and/or methane in the moderator system so much nitrogen will be added in front of the gas outlet that the outcoming gas mixture is not explosive.

During the first trial the moderator vessel had been filled with 850 ml water and refrigerated down to temperatures of 9 K at the bottom and 13 K at the top of the moderator vessel. With a heater that had been integrated on the top plate of the cold head, we were able
to change the temperatures and to provide moderator temperatures up to 90 K. Figure 6 shows the measured temperatures at the bottom and at the top of the moderator vessel first without heating the top plate of the cold head, secondly by heating the cold head more and more. All the time the temperature difference between the top and the bottom of the vessel was about 4.0 K.

![Figure 6: Temperatures at the moderator vessel](image)

4. CONCLUSION

It has been demonstrated which engineering efforts were necessary to install the cryogenic moderator system for JESSICA, a full scale model of the target-reflector-moderator system for a large spallation source. The cryogenic moderator system has been installed and improved. The moderator system can be operated with different moderator materials like water, ice, methane hydrate, methane, hydrogen, and a combination of different moderator
materials. This is possible because the moderator system can be operated both as a closed system and as an open one, where a liquid or solid medium can be filled into the moderator vessel under helium atmosphere.

So far, experiments at JESSICA have been performed with water, ice and methane hydrate as moderator material. The measured energy spectra of these moderator materials are documented in [4] and [5].

Additional experiments at JESSICA will be made with moderator material which has to be condensed from storage containers into the moderator vessel. These experiments with hydrogen and methane will take place in 2003.

ACKNOWLEDGMENTS

The authors are grateful to the whole JESSICA collaboration. The staff members of the Central Department of Technology are acknowledged for building up JESSICA. In particular F.J.Bongartz and M.Dick are acknowledged for their good ideas in realizing difficult technical details of the cold moderator. Moreover, we acknowledge the work in preparing the technology of the cold moderator system by H.Barnert-Wiemer and we thank N.Paul for the help in building up JESSICA at the COSY accelerator.

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Experimental studies of neutronic characteristics of hydrogen moderators at para rich concentrations and comparison with calculations

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ABSTRACT

Hydrogen is the most important material as a cold neutron moderator for the future high power spallation neutron sources. However, experimental data for the moderators of hydrogen with high para concentration are very scarce and not suitable for design of the future moderator system. We made equipments to convert ortho to para-hydrogen and to measure the ortho/para ratio. After that, we measured the neutronic performance of the hydrogen moderators with 5 cm thickness and compared with simulation. The results indicated that overall characteristics of the experimental result agreed with the calculated results but there exist difference in the absolute values. Therefore, the simulation is useful for the basic design but experiments are necessary to evaluate the precise neutronic performance.

1. INTRODUCTION

Hydrogen is used as cold neutron moderator for the Japan spallation source and also in the spallation neutron source in the USA. The hydrogen consists of para and ortho-hydrogen and the neutronic performance is different between them since the neutron cross section below about 20 meV is very different. Neutron is transparent below about 10 meV for the para-hydrogen due to the very low cross section of para-hydrogen. Simulation calculation is very important for the design of the cold moderator. The simulation results showed that the para rich hydrogen moderator gave better neutronic characteristics than the normal hydrogen[1]. In the decoupled moderator a para-rich moderator gives narrow pulse width higher pulse peak intensity and in the coupled moderator the para-rich moderator gives higher integrated neutron intensity by using the thicker moderator with keeping the pulse shape good. Such features are very useful for the neutron scattering experiment.

However, the neutron cross section of the para-hydrogen is complicated since it has coherent like nature of the scattering although hydrogen is essentially incoherent. Therefore, synthesis of the cross section is not so easy. Furthermore, the validity check is not performed sufficiently since the experimental cross section data and spectrum data are not enough and have not given sufficient information.

Therefore, it is very important to check the validity of the simulation results by the experiments. Here, we present experimental results of the para-rich hydrogen moderator as well as equipments to convert ortho to para and to measure ortho/para ratio. Comparison with simulation is also mentioned.

2. EXPERIMENTAL

At first we have to make an equipment to convert ortho to para since the conversion time is too long, about 43,000 hours even at 20 K. We used catalyst of 30% of Al2O3 and 70% of Cr2O3 at first, and later Fe(OH)3. The system we used is indicated in Fig. 1. Hydrogen gas is...
supplied from the high pressure bombe and cooled down to about 20K in the cryostat maintaining the catalyst. Here, we get para concentration of equilibrium at temperature. We controlled the para concentration by the temperature at the catalyst since we supposed that the para concentration became equilibrium value at that temperature. The gas is transferred to a moderator chamber and condensed there.

Figure 1. Flow diagram of the hydrogen gas to convert ortho to para.

The para rich gas was sampled from the line to measure the ortho/para ratio. We used a simple method using a principle measuring the voltage caused by the difference of the thermal transmission between different para ratio hydrogen gasses in the Pirani gauges. The system is shown in Fig. 2 and the procedure is as follows:

Figure 2. Equipment for measuring ortho/para ratio
Step 1: Normal gas is filled in both Pirani gauges and the bridge circuit was adjusted so as to diminish the electromotive force.

Step 2: Normal gas in one of the Pirani gauges is exchanged by sample gas.

Step 3: \( V \) is measured.

The voltage measurement was performed at a hydrogen pressure of \( 5.3 \times 10^3 \) Pa. We have to make calibration curve of voltage vs. para-ratio before hand. The accuracy of this measurement is not clear now but it may be less than 2-3%. We intended to check the accuracy by using Raman spectroscopy.

Neutron measurements were performed at Hokkaido linac facility. The target-moderator-reflector system (TMRS) is shown in Fig. 3. Pb was used as a target and graphite as a reflector. The moderator size was 5 cm thick, 12 cm wide and 12 cm high. For a coupled moderator a 15 mm thick polyethylene pre-moderator was placed instead of Cd decoupler. Temperature of the hydrogen moderator was about 17 K. We measured the energy spectra for a coupled and a decoupled moderators with the time of flight method.

Figure 3. Experimental setup of TMRS.

For the simulation we used the MCNPX code with using the ENDF-B/V and VI cross section data, and the TMRS model for simulation included the main part of the experimental setup which affected the neutronic performance.

3. EXPERIMENTAL RESULTS AND COMPARISON WITH SIMULATION

Energy spectra from the decoupled moderator are shown in Fig. 4 as well as the simulation results. The para ratios examined were 35 and 99%. The simulation results give higher intensities than the experimental ones. The intensity is different around 0.005-0.3 eV. The intensity ratio is shown in Fig. 5. The intensity ratio is defined here (Intensity at any para concentration)/(Intensity at 35% para concentration). The overall tendency of the simulation is almost the same as that of the experiment.

The intensity ratio around 0.01-0.1 eV agrees well although the absolute intensity around there was different, and little bit different below 0.01 eV. One of the reasons of the difference would be the difference between temperatures of experiment and calculation. We only have cross section data at 20K but the experiment performed at 17K. Therefore, we took into account only the density change of the hydrogen in the calculation. Error in the measurement of the para concentration may also be another reason.
Next, we measured the energy spectra from the coupled moderators at 35, 60, 90, 95 and 99% para concentration. The experimental results are shown in Fig. 6 and the results of the simulation are shown in Fig. 7 as a reference. In both figures intensity ratios are also indicated. The energy spectra change very much depending on the para ratio. The decrease in the intensity ratio from 0.015 to 0.1 eV is larger in the simulation compared with the experiment, and on the other hand the increase in low energy region below about few meV is large in the simulation although the overall feature is similar each other. The large decrease in the intensity below 1 meV in the experiment may give some doubt about the intensity gain of the thick para hydrogen moderator speculated from the simulation result. Para hydrogen is transparent below about 10 meV. Therefore, effect of surrounding materials would not be negligible and we have to take into account all things affecting the neutronic performance. But, it is not easy in calculation since we define tallies only we think them necessary. Anyway, we need careful experiments simulating the planned TMRS in detail to confirm the neutronic performance obtained by the simulation calculations.

Figure 4. Energy spectra from decoupled moderators of 35 and 99% para-hydrogen.

Figure 5. Comparison of intensity ratios between experiment and simulation.
4. CONCLUSIONS

We performed measurements on the neutronics of the coupled and the decoupled moderators at different para concentrations and compared them with the simulation results. The spectra change very much depending on the para ratio, which tendency is almost similar to the results of the simulation but the absolute spectrum intensity and the intensity ratio depending on the para ratio are different from the expected value of the simulation. The coupled moderator seemed to be affected by surroundings more strongly than the decoupled moderator. We need careful experiment to get the precise neutronic performance of the future project.

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The JESSICA Experiment – Part II: Results from the JESSICA-Experiment

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ABSTRACT

In this article we like to report on the latest results of the JESSICA experiment. We focus on the experiments with an ice moderator at 20 K and 70 K. The measured time of flight spectra and the derived energy spectra will be presented. For the ice moderator we will show also the time of flight spectra for specific wavelengths. For the first time we investigated the moderation properties of a methane-hydrate moderator in a realistic environment. We compared this new data with the previous obtained ice data.

1. INTRODUCTION

With the JESSICA experiment (Jülich Experimental Spallation Target Set-up In COSY Area) we like to study new moderator materials in a realistic environment. For this reason a target, moderator, and reflector system was constructed based on the ESS (European Spallation Source) reference design from 1996 [1]. More detailed information about the experiment can be found in a further contribution to this meeting [2]. In this article we like to focus in more detail on the cold moderator experiments carried out until now. After finishing the start-up phase of the experiment using an ambient temperature water moderator we continued our experimental program with an ice moderator at 20 K and 70 K. We compared the results with the previous water measurements to study the influence of the decreased temperature on the energy spectra as well as on the time of flight spectra for selected wavelengths. By comparing our data with older experimental data, carried out by K. Inoue [3,4] and A.W. McReynolds and W.L. Whittemore [5,6], we checked if our experiment would deliver reasonable data. However a direct comparison with these data is not possible because of various geometries of the investigated systems and different moderator configurations. Also the process of neutron production is diverse. In our experiments a 1.3 GeV proton beam hits the mercury target and neutrons are produced via a spallation process. In case of the older experiments, an electron beam hits a heavy metal target and the bremsstrahlung creates photo neutrons.

For the first time we studied a methane-hydrate moderator. The obtained energy spectra will be shown. Unfortunately the statistics for the time of flight spectra for specific wavelengths was to low and could not been analyzed.
2. TIME OF FLIGHT SPECTRA AND ENERGY SPECTRA FOR WATER AND ICE

The time of flight spectra are obtained in two steps. The first measurement counts all neutrons leaving the moderator including background. To eliminate the background a further measurement is performed. In this second measurement only those neutrons are detected, which are not absorbed in an additionally inserted Cadmium layer in front of the neutron flight path. The high neutron absorption cross-section of Cadmium for thermal neutrons prevents them to reach the detector. The difference of both spectra results in the time of flight spectrum for the thermal neutrons. Fig. 1 shows the time of flight spectra of thermal neutrons for a water moderator at different temperatures. The data are normalized to the detector area and the number of incident protons per pulse. It can be seen that the spectra of the ice moderators are shifted towards longer flight times compared to the spectrum of a water moderator at room temperature.

![Figure 1](image1.png)

**Figure 1.** Time of flight spectra of a water/ice moderator at 300 K, 70 K, and 20K.

![Figure 2](image2.png)

**Figure 2.** Time of flight spectrum of an ice moderator at 20K measured at JESSICA (left graph). Neutron time of flight spectra for different moderator materials measured by Whittemore and McReynolds (right graph).
Similar time of flight spectra were measured by W.L. Whittemore and A.W. McReynolds [5,6]. Because they used also an ice moderator at 21 K it was interesting to compare their results with our experiments. It is important to note that the used geometry of the moderator was different. This means a direct comparison of both experiments is not reasonable. Fig. 2 shows again the time of flight spectra of a 20 K ice moderator and the measured time of flight spectra from Whittemore and McReynolds. The spectra labeled with (1) and (2) are for ice at 21 K. The difference between two spectra is that for (1) the detector looks into a reentrant hole whereas for (2) the detector views the shell surface of the cylindrical moderator. JESSICA uses a rectangular moderator box (10 cm x 12 cm x 5 cm) without a reentrant hole. This is a similar geometry as spectrum (2) shown in the right graph of Fig.2. When comparing our results - the length of the neutron flight path was 5.40 m - with spectrum (2) we observe the same characteristics of the shape of the time of flight spectra.

Other publications [e.g. 3,4,5,6] prefer to show the energy spectra of the neutrons leaving the moderator. To be able to compare the results obtained with JESSICA with those data the time of flight spectra have to be transformed into energy spectra. For this reason we use the following transformation:

\[ i(t) dt = \frac{i(t(E)) dt}{dE} dE = I(E) dE \]  

(1)

With:

\[ E = \frac{m \cdot v^2}{2} = \frac{m \cdot s^2}{2 \cdot t^2} \Rightarrow t^2 = \frac{m \cdot s^2}{2 \cdot E} \Rightarrow t(E) = \sqrt{\frac{m \cdot s^2}{2 \cdot E}} \]  

(2)

And the derivation of \( t(E) \):

\[ \frac{dt}{dE} = -\frac{m}{\sqrt{2 \cdot E \cdot \sqrt{E}}} \]  

(3)

The energy spectra can be written as:

\[ I(E) = \frac{i(m \cdot s^2)}{2 \cdot t^2} \cdot \sqrt{\frac{m}{2 \cdot E \cdot \sqrt{E}}} \cdot s \cdot \sqrt{\frac{m}{2 \cdot E \cdot \sqrt{E}}} \]  

(4)

Figure 3. Energy spectra of water at 300 K (filled squares), ice at 70 K (filled circles), and ice at 20 K (filled triangles). The data are only normalized to the number of incident protons and detector area.
When applying this transformation to the measured time of flight spectra we obtain the energy spectra of the neutrons leaving the moderator. A comparison of the energy spectra for water at 300 K, ice at 70 K, and ice at 20 K is shown in Fig. 3. These spectra are not corrected for dead-time and the time distribution of the moderation process.

The presented data in Fig.3 are only normalized to the number of incident protons and the active detector area. We like to point out the spectra are not normalized to the 1/E-slope but shown in their absolute values. The accordance of the 1/E-slope is remarkable. The shift of the spectra to lower neutron energies for colder moderator temperatures is evident. Similar experiments were performed by Inoue et al. [3,4]. Fig.4 illustrates the published energy spectra for water/ice moderators at several temperatures.

![Figure 4. Energy spectra of water/ice at several temperatures measured by Inoue et al. [3,4].](image)

Comparing these spectra with the spectra measured at JESSICA it can be recognized that the shapes of the energy spectra of both experiments in principal are in accordance. When normalizing the JESSICA data to 10 at 1 eV we observe same differences. The JESSICA measurements show a slightly lower slope in the 1/E-region. We suggest that this is an effect of the counting rate reducing cadmium aperture which is less effective for neutron energies above 0.4 eV. Larger deviation we observe at the maximum. This is due to the reentrant hole in the cylindrical moderator used by Inoue et al.. However the typical structure in the energy region between 0.01 eV and 0.1 eV can be seen also in our measurements. Whether we use a different moderator geometry in our experiments the comparison with older measurements demonstrates that with JESSICA reasonable results can be obtained. From these spectra we determined the effective moderator temperature. This was a check, if the experiment will be sensitive to changes of the moderator temperature. The determined values are listed in Tab.1. For the determination of the effective moderator temperature we assume a Maxwell distribution of the energy range of the maximum.
Table 1. Real moderator temperature compared with the determined effective moderator temperature.

<table>
<thead>
<tr>
<th></th>
<th>Water 300 K</th>
<th>Ice 70 K</th>
<th>Ice 20 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Real temperature as measured</td>
<td>300 K</td>
<td>70 K</td>
<td>20 K</td>
</tr>
<tr>
<td>Effective moderator temperature determined from experiment</td>
<td>343±14.7 K</td>
<td>110±2.2 K</td>
<td>71±4.0 K</td>
</tr>
<tr>
<td>Effective moderator temperature determined from MC-simulation</td>
<td>309±10.2 K</td>
<td>120±2.5 K</td>
<td>63±1.6 K</td>
</tr>
</tbody>
</table>

The first result is, that we see the decrease of the temperature also in the data. But the effective moderator temperature determined from the experimental data as well as those from Monte-Carlo simulations results in higher temperature especially for ice than the real temperature. Whereas the above-mentioned assumption is correct for water, it is no longer valid for an ice moderator resulting in higher effective temperatures. A further reason is that we measure the neutrons leaving the outer surface of a rectangular moderator box. The maximum of the determined spectrum is shifted to higher energies than compared with a spectrum measured while viewing the moderator through a reentrant hole.

3. WAVELENGTHS DEPENDENT TIME OF FLIGHT SPECTRA FOR WATER AND ICE

The wavelengths dependent time of flight spectra are measured applying the method of Bragg reflection. A pyrolytic graphite crystal was moved into the neutron flight path selecting wavelengths of $\lambda/1=4.74\text{ Å}$, $\lambda/2=2.37\text{ Å}$, $\lambda/3=1.58\text{ Å}$, $\lambda/4=1.19\text{ Å}$, and $\lambda/5=0.95\text{ Å}$. These neutrons are counted with a neutron detector located in a second neutron flight path perpendicular to the direct neutron flight path. In Fig. 5 the wavelength dependent time structure for water at 300 K and ice at 70 K and 20 K is illustrated.

![Figure 5](image-url)  
**Figure 5.** Wavelength dependent time structure for water at 300 K and ice at 70 K and 20 K.

Here also the shift of the energy spectra towards lower energies, longer flight times respectively, can be observed. Whereas the peak intensity at 4.74 Å increases with lower temperatures the intensity e.g. at 0.95 Å is lower the lower the moderator temperature is. These
data were analyzed in more detail. We determined the peak width at FWHM and the decay constant. The values are listed in Tab.2.

Table 2. Peak widths and decay constants for water at 300 K and ice at 20 K for different wavelengths.

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>300 K</th>
<th>20 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95 Å</td>
<td>Peak width at FWHM in µs: 50 µs, 60 µs, 90 µs, 100 µs</td>
<td>Peak width at FWHM in µs: 30 µs, 50 µs, 90 µs, 280 µs</td>
</tr>
<tr>
<td>1.19 Å</td>
<td>0.018±12%</td>
<td>0.057±12%</td>
</tr>
<tr>
<td>1.58 Å</td>
<td>0.016±6%</td>
<td>0.039±12%</td>
</tr>
<tr>
<td>2.37 Å</td>
<td>0.014±7.5%</td>
<td>0.019±9%</td>
</tr>
<tr>
<td>4.74 Å</td>
<td>0.015±10%</td>
<td>0.005±8%</td>
</tr>
</tbody>
</table>

4. ENERGY SPECTRA OF A METHANE-HYDRATE MODERATOR

For the first time we investigated a methane-hydrate moderator. The basic idea of such a moderator is to combine the spectral properties of ice and solid methane resulting in higher neutron intensity over a broader energy region. This will help to increase the neutron current of a spallation neutron source by a factor of two to three. With the JESSICA experiment we like to validate this presumption.

Figure 6. Energy spectra of methane-hydrate (triangles) and ice (circles) at 20 K. The right diagram shows the energy spectra with background correction whereas the left picture illustrates the same spectra without background correction.

At JESSICA a methane-hydrate moderator at 20 K was investigated. In figure 6 the energy spectrum of a methane-hydrate moderator is plotted compared to the spectrum of an ice moderator at 20 K. The left picture shows the comparison of the energy spectra without background correction (assuming a constant background), the result being very promising. It can be seen that the methane-hydrate data are very similar to ice in the energy range above $1 \times 10^{-2}$ eV. For lower energies a gain of a factor of two can be seen. But unfortunately the results looks quit different when subtracting the background obtained with a cadmium measurement. The gain in the energy range below $4 \times 10^{-3}$ eV is still visible, but for energies...
between $4 \times 10^{-3}$ eV and $2 \times 10^{-1}$ eV the methane-hydrate moderator is inferior to an ice moderator. We like to remark, that the shown energy spectra are only normalized to the number of incident protons and the active detector area, but neither to the hydrogen density nor to the mass density.

5. CONCLUSION

In this article the latest results of the JESSICA experiment were presented. We measured the time of flight spectra for water and ice at different temperatures. From the time of flight spectra the energy spectra were derived. In the future we will compare the data with Monte-Carlo simulations using new neutron scattering kernels [7]. First measurements with a methane-hydrate moderator delivered promising results but have to be confirmed with further measurements. Especially the background effects will be studied in more detail using a neutron generator. The experimental investigation of the wavelength dependent time structure of the neutron pulses will be performed during the upcoming beam time.

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[7] W.Bernnat et al., Scattering kernels of cryogenic media; this conference
1. INTRODUCTION

Cases of spontaneous release of energy ("burp") were observed numerously in solid methane, water ice and other hydrogenous compounds irradiated in fast neutron fields with absorbed dose 2-10 MGy [1-6]. Nature of this phenomenon is that accumulation of radicals and thermal instability of a sample under due concentration of radicals culminate to autocatalytic reaction of their recombination. The most odious feature of this phenomenon is that irradiation time, before a burp occurs, varies significantly even in identical irradiation condition. Respectively, amount of released energy varies as well. For example, in URAM-2 experiments [5,6] with water ice, irradiation time before appearance of spontaneous burp varied from 5 hours to 11 hours for equal samples and up to 20 hours for the smallest sample. Another feature of the phenomenon is that regularities for occurrence of spontaneous release of energy (that is, dependence on temperature, size of sample, absorbed dose) can’t be extracted explicitly from experimental data, if applying known relations for critical concentration of radicals, namely: Semenov’s and Frank-Kamenetski’s conditions of thermal instability of a sample [7], Jackson’s relation for chain process of recombination of uniformly distributed radicals [8], critical condition based on accounting for acceleration of a process of recombination in the regions of micro-cracks [9-11], and, finally, critical condition for irregular distribution of radicals proposed by the author of this article [4,12,13]. Not one of these theories predicts casual character of a burp on macro-scale basis.

So that, notwithstanding fair amount of experimental data on spontaneous burps, it is still impossible to derive well-balanced theory of this phenomenon. One attempt to understand a reason for the strange behavior of spontaneous burping is a probabilistic, cluster model of spontaneous release of energy, developed in the Chapter 4 of this paper. Spontaneous burps observed during URAM-2 project and in solid methane moderators of the neutron sources in operation are analyzed from this standpoint.

2. DISCUSSION ON EXPERIMENTAL DATA OF SPONTANEOUS BURPS

2.1. Solid methane

Among 27 irradiations of solid methane samples made in the frame of the URAM-2 project, only one spontaneous burp occurred (in 5 mm shell sample after 11 hours). No other spontaneous burp was observed even for bigger samples and longer irradiation though there were at least 8 irradiations when such event should be expected relying on the previous experience with solid methane moderators operation [1-4, 16, 17]. Conditions were almost identical (regarding irradiation temperature, absorbed dose, cooling condition) in URAM-2 and in cold moderators at IBR-2, IPNS, and KENS facilities where spontaneous burps were recorded. It is significant that in URAM-1 experiments [16] where mass of methane was small (about 16 g) no spontaneous burp was also registered.
First of all, we should conclude that characteristic size of a sample (which was smaller at URAM-2 than in IBR-2 or IPNS moderator) hardly affects critical condition for burping. Really, computer simulation of thermal instability by a model, accounting for a size of a sample (the case of thermal diffusion model of recombination of uniformly distributed radicals, Frank-Kamenetski’s case (See in [4, 18]) showed, that relation between released energy in induced burps and temperature of ignition is very steep (see Fig. 1) for a complete choice of set of parameters ensuring generation of a burp, that are $K_2, R, T_{2act}$ (see Eq.1 in [5] presented at this meeting). No case displays linear character of $Q(T)$ relation in the broad range of 10 K in contrary to the URAM-2 case, see Fig. 6 in [5]. Moreover, it is known (see, for example, [1, 4, 14, 18]) that thermal instability in the thermal diffusion model depends on cooling time of a sample: the longer cooling time, the less stability. Though cooling time of the cold moderator of IPNS (60 sec) is less than that of a sample No 23 at URAM-2 (90 sec), no spontaneous burp occurred in the latter case.

![Figure 1](image.png)

**Figure 1.** Relation between stored energy and $T_{ign}$ evaluated with Frank-Kamenetsky’s model of thermal instability.

Explanation of infrequent occurrence of spontaneous burps at URAM-2 experiments with solid methane samples may be done applying a model of fast recombination of radicals accounting for non-uniformity of radical spatial distribution, [4, 8, 12-14], complemented with a probabilistic approach to burp occurrence.

For the moment, we apply for URAM-2 and ESS condition a simplified relation between critical stored energy and irradiation (or ignition) temperature $T_0$ [18]:

$$Q_{crit} = \frac{2 \cdot c_{methane} \cdot (T_{cl} - T_0)}{\gamma}$$  \hspace{1cm} (a)

There are two free parameters in the simple model – $T_{cl}$ which is interpreted as temperature of ignition of a “burnable” cluster (a small region such that small perturbation of temperature - several track superposing the region or self annealing of a structural defect - can stimulate recombination of all radicals in the region), and $\gamma$ factor which is a fraction of clus-
tered radicals. But in more sophisticated mathematical versions of the model it should be referred to as a factor of a grade of non-uniformity, that is, the more probable appearance of a burnable region, the higher $\gamma$ factor. The fact that energy released in induced burps in URAM-2 is linear to temperature of ignition (see Fig.6 and Eq.(4 ) in [5]), may confirm validity of this model. To satisfy experimental results of induced burps in URAM-2, $\gamma$ factor should be put equal to about 0.4. According to the simplified model, maximum value of $\gamma$ factor is equal to unity

Initiation of a burp in the conception of non-uniformity of radical distribution is independent on a size of a sample. Really, ignition was always instantaneous over a sample which testifies to the statement above. But, propagation of a process of recombination through the sample is only possible until length of recombination wave $\sqrt{\chi \tau}$ ($\chi$ is temperature diffusivity and $\tau$ is a reaction time) is less or comparable to a characteristic size of a sample. From the given experiment, $\tau \leq 1$ s, and length of recombination wave is then less than 0.6 mm. Really, 0.3 mm thick of a sample was observed to be a limit size for a burp occurrence.

But a conclusion made in the previous paragraph is far from being true for a volume of a sample. This is proven in the Chapter 4 of this paper. Really, Eq. (a) defines condition for initiation of fast recombination process, that is, defines local condition. That means that in some local place, at some moment, density of radicals and local temperature satisfies to chain reaction of recombination. Undoubtedly, probability of an appearance of local, burnable configuration of radical distribution and of high local temperature increase linearly with volume of a sample, see Eqs. (3), (7) in Chapter 4. Therefore, to keep Eq.(a) valid, we must consider $\gamma$ factor be depending on absorbed dose and volume of a sample (just volume, not characteristic size). Moreover, this factor may vary from one experiment to another. Variations are less for bigger samples, in accord with a deduction made in section 4.5. So that, one may consider both $\gamma$ factor and $Q_{crit}$ in Eq.(a) only as averaged, expected values for an individual burp.

Then, it is reasonable to assume that $\gamma$ factor in Eq.(a) for big samples such as cold moderators of IPNS, KENS, and IBR-2 (their volume of solid methane one hundred times more than volume of URAM-2 capsule) is higher than 0.4. Critical concentration for solid methane cold moderators is about 50÷60% of that for URAM-2. Then, critical condition for burping with Eq.(a) would be close to reality if putting $\gamma$ factor equal to 0.8÷1 and keeping $T_c$ parameter the same, that is 36K.

2.2. Water ice

First of all, it is worth to say that water ice samples display spontaneous burping more “readily” than methane, but a stochastic character of burps remains. Only four of six samples, irradiated at the same condition, displayed spontaneous burps. Irradiation time to spontaneous burping at 20-25K varied from 5 to 10.5 hours (for segmented samples >2.2 g) with difference of critical concentration of radicals up to 50%.

Two reasons for stochastic character of burping in water ice can be supposed: probabilistic character of ignition of recombination process and structure of a sample. Temperature conditions during preparation of ice samples differ a little bit, and, probably, affect structure or texture of ice. A number of defects in a sample can affect a rate of diffusion of radicals, or dispersion of density of radicals. In the cluster, probabilistic model of the process of fast recombination this means changes in burping conditions.

Due to dispersion of critical concentration of radicals it was impossible to determine the temperature-critical concentration of radical relationship correctly. The only conclusion is that this relationship is very weak in the range 20-30 K:

$$r = Q_{crit}(30K)/Q_{crit}(20K) < 1.4.$$
The equation (a) may also describe condition for spontaneous burping in ice, with the same constraints as for solid methane. In this case, \( \gamma \)-factor is about 0.1. Applying formulas (5) and (6) from [5], we get a temperature condition for probability to have a spontaneous burping in ice (for higher temperature, saturated density of radicals is lower than critical one):

\[ T < 35 \, \text{K} ÷ 36 \, \text{K}. \]

Actually, no burp were observed at \( T > 34 \, \text{K} \). But, accounting for the uncertainty of critical condition because of variation of time to burping, one can expect a burp even at higher temperature, may be, up to 40 K.

It is interesting to note that critical density of radicals in water ice increases with temperature in the range 20-34 K. Such behavior contradicts to thermal diffusion model of recombination as in the latter case it should go down with temperature, see Fig.1 and [4,7]. In cluster model it is easy to understand with an eye to linear dependence of \( Q_{\text{crit}} \) on specific heat of ice (Eq. (a)), which goes up steeply in the range 20K-40K [15].

A lack of spontaneous burps in beads of ice prepared by cooling water in liquid nitrogen (we call such prepared ice «amorphous», though it is sooner crystalline with many defects) can be explained by short time of irradiation and too high irradiation temperature. Most probably, it would occur at 20-25K as it was for hydrates (see in the relevant section of [5]) after 15-20 hours of irradiation, when stored energy exceeds 90-100 J/g.

3. ANALYSIS OF BURPING OF MODERATOR MATERIALS IN ESS CONDITION

3.1 Burps in solid methane moderator

Basing on URAM-2 experiments analysis one can conclude that saturation curve for ESS solid methane moderator may be restored by Eq.1 in [5] with \( R \) depending on time and without the second order term. Calculated saturation curves are shown in Fig. 2 for four irradiation temperatures. It was assumed that \( D^* = 2 \, \text{W/g} \) and radical recombination reaction is \( \text{H} + \text{CH}_3 \).

![Figure 2. Saturation curves of stored energy in an ESS solid methane pellet for a set of irradiation temperatures. Straight lines point to critical values of Q.](image-url)
Due to high dose rate and big volume, uncertainty of time to burping for the ESS moderator is negligibly small. Applying for the ESS the cluster model, given above, we assumed $\gamma \approx 0.8 \div 1$ in Eq.(a) because volume of ESS moderator chamber is as big as of IPNS. By comparing saturation curves for the ESS, Fig. 2, and critical condition by Eq.(a), one can calculate a duration of irradiation until spontaneous burp occurs in one of solid methane beads as a function of irradiation temperature. This value which is commonly referred to as ‘maximum reliable residence time’ of beads, is shown in Fig. 3 for magnitudes of $\gamma$ between 0.8 and 1 (upper and lower border lines of the gray area).

Challenging question is: would a recombination wave propagate from one bead to another? Most probable, yes, because under-heating of methane to the temperature of ignition, being irradiated at 21K, (see Fig. 6 in [5]) is only 2.5K. Released energy in spontaneous burp at 21K is expected to be (Fig. 2) about 60 J/g, and maximal temperature of a bead is 60 K accordingly. Transient superheating of a contact area between two adjacent beads can be estimated in the first approximation by a simple relation

$$\delta T \approx (T_{\text{max}} - T_{\text{LH}}) \frac{t_{\text{cool}}}{\tau_{\text{burp}}},$$

where $t_{\text{cool}}$ is a cooling time of the contact area ($t_{\text{cool}} \propto (\rho c_p)_{\text{methane}} h/\alpha$, where $h$ is a cross size of the contact area, $\alpha$ is a heat transfer coefficient) and $\tau_{\text{burp}}$ is duration of a burp, 0.5-0.6 sec. Assuming heat transfer coefficient near contact area between two adjacent beads (where liquid hydrogen is almost stagnant) be close to $10^2$ W/cm²/K (experiments in Oak-Ridge on cooling of methane beads), we have

$$\delta T [K] \approx (0.5 \div 1) \times 10^4 h (\text{h [cm]}).$$
Even at \( h = 0.01 \text{ mm} \) which is too small value for a bead of 2 mm diameter,

\[ \delta T \approx 5 \pm 10 \text{ K}. \]

This estimate proves high probability of recombination wave propagation from one bead to another. Moreover, this statement is confirmed by interaction with the URAM-2 experiments with beads of methane hydrate and beads of ice in argon matrix where ignition of burps occurred always in a whole pack of beads. Actually, taking in mind that thermal conductivity of solid argon is much better than that of liquid hydrogen, one may conclude that cooling of interface between two beads in the case of stagnant liquid hydrogen is worse than in the case of solid argon (calculation of thermal expansion of ice beads in solid argon matrix showed that at 20 K beads are compressed in the matrix). Then, temperature rise in a contact area should be higher in liquid hydrogen, and propagation of recombination wave from one bead to another would come easier.

If one accepts mechanical nature of propagation (“percolation” as it is defined in [11]) of ignition of clusters of radicals, then positive answer for the question “would a recombination wave propagate from one bead to another?” would be evident.

And the last pessimistic conclusion: Even if one assumes that no spontaneous burps is expected in ESS solid methane moderator cooled with liquid hydrogen, any small perturbation of temperature in any single bead (+2\( \pm \)3K) can cause fast recombination process in a whole assembly resulting in evaporation of cooling hydrogen.

3.2 Burps in water ice for ESS irradiation condition

For the ESS moderator conditions for spontaneous burping in ice can be derived from URAM-2 data with correction for higher dose rate and big volume of ice. Time to burping will be 9.3 times less according to dose rate (for 1 MW ESS target station) and dispersion will be much less. Unlike the solid methane case, \( \gamma \)-factor for big samples of water ice is unknown. But one statement is evident: critical concentration of radicals (or amount of stored energy) can’t be less than minimal concentration to make an induced burp, which is 65-70 J/g. Accepting this value, we have \( \gamma \approx 0.15 \).

Estimated values of times between succeeding spontaneous burps in small samples of ice prepared by slow freezing of pure water (diameter < 30 mm) versus temperature are given in Fig. 4. Because of dispersion in burping condition, there are two curves \( t(T_{irr}) \), and expected times are confined between them. For the case of the ESS ice moderator (many beads) only lower curve should be taken into account. Released energy in spontaneous burps will be 65-70 J/g, and the sample will be heated up to 130 K. Samples of ice prepared by freezing water in liquid nitrogen (diameter \( \sim \) 5 mm) would behave, probably, like hydrates but this is not fully confirmed.

3.3 Burps in hydrates for ESS irradiation condition

For the ESS moderator made from THF or methane hydrate ice one can expect the next burping condition:

- temperature is less than 25 K,
- time between succeeding burps - 1.4\( \pm \)1.6 hour,
- stored energy \( \geq \) 80-100 J/g,
- heating - up to 170 K.
4. PROBABILISTIC MODEL OF SPONTANEOUS RELEASE OF ENERGY (“BURP”) IN IRRADIATED ICES

4.1 Conception of the model.

A basis of this model was outlined in previous papers of the author [12,13]. There it was stated that a key to understand features of fast spontaneous reaction of recombination of radicals (SB) is in taking into account irregularities in space distribution of radicals and in energy deposited. Radicals are generated in the tracks of recoil protons, and therefore, they are arranged mainly in lines or in spurs. Because diffusion of radicals at low temperatures (10-30K) is too slow to get them away from their origins, we come to the conclusion about non-uniform distribution of radicals and their concentration in clusters. Besides their original distribution due to tracks formation, clusters of radicals may occupy structure defect sites as well. Structure defects can be caused by radiation or generated in the course of freezing of a sample. Two-dimensional computer simulation of proton track distribution revealed high dispersion of concentration of radicals on a small scale base: three-fourfold increase in local density of radicals as compared to averaged over a sample [12]. As rate of recombination reaction is square proportional to density of radicals, such increase in local density of radicals may lead to initiation of auto-catalytic reaction in this local area of high density of radicals. Therefore, clustered structure of distribution of radicals decreases critical density of radicals as compared to those determined by thermal instability of a sample.

A simplified mathematical approach to this model was derived in [18] with no account to a stochastic character of initiation of a burp. This paper gives more detailed insight into the
model and some consequences of its application. It explains why process of SB has a stochastic character.

In the basis of the model we have put three qualitative conditions for SB appearance which are necessary and sufficient:

1. In a sample under irradiation, there exist clusters of radicals highly enriched with radicals occupying a tiny region of definite size (let us call such clusters “burnable”): both density of radicals and size of the clusters are big enough that any perturbation (“ignition”) inside the cluster actuates recombination of all radicals inside the cluster and, beside that, an amount of heat released in the burnable cluster can trigger a process of penetration of recombination reaction beyond the cluster.

2. The second condition is appearance of a source of ignition, a kind of “detonator”, a “match”, which stimulate recombination in the burnable cluster.

3. And, finally, space-averaged density of radicals over the sample, size of the sample, and cooling condition are that which can sustain propagation of recombination reaction through the sample, either in the form of a wave of recombination or in the form of soliton-like temperature spikes.

The last condition is widely used in literature of chemical kinetics and it is suffice to say that in the cases of the current interest (solid methane at 20-30K, water ice at 20-40K, used as cold neutron moderators) this condition is satisfied usually earlier in the course of irradiation than the first two (except too small samples). Therefore, the first two conditions are most significant to study.

4.2 General approach.

Let us denote density of radicals in a “burnable” cluster by \( n_0 \), averaged volume of a burnable cluster by \( V_0 \), volume of a sample by \( V \), space-averaged density of radicals over the sample by \( \bar{n} \). Then, number of burnable cluster concurrently existing in the sample at the instant \( t \), may be expressed in the form:

\[
N(t) = p(n_0, V_0, \bar{n}, t) \frac{V}{V_0}
\]

where function \( p(n_0, V_0, \bar{n}, t) \) is probability that volume \( V_0 \) chosen at random appears to be a burnable cluster. Sure, \( n_0 \) and \( V_0 \) are, to some extent, not strictly defined, though, they are bounded in definite ranges of values. We imply \( n_0 \) and \( V_0 \) to be equal to averaged values in the ranges. If “life time” of a burnable cluster is denoted by \( \tau_s \), then probability of SB appearance in unit time is

\[
P = p(n_0, V_0, \bar{n}, t) \frac{V}{V_0}/\tau_s
\]

and mean expectation time to burping at the instant \( t \) is

\[
T_{SB} = \frac{1}{P} = \frac{V_0 \cdot \tau_s}{p(n_0, V_0, \bar{n}, t)/V}.
\]

It is most probable to assume that burnable clusters are ignited with a hot track of proton or, which is more probable, with some superimposed tracks. Then, the “life time” of a burnable cluster \( \tau_s \) can be expressed as

\[
\tau_s \sim \frac{1}{(V_0 \bar{D})}.
\]
where $\bar{D}$ is absorbed dose rate. Now, a mean expectation time to burping at the instant $t$ appears to be proportional to:

$$T_{SB} \sim \frac{1}{p(n_0, V_0, \bar{n}, t) / (V \bar{D})}$$  \hspace{1cm} (3a).$$

It is important: even this quite general relation with uncertain parameters $n_0, V_0$ says definitely that appearance of SB is inverse proportional to volume of a sample, not characteristic size or geometry of a sample, as it is for thermal instability conditions. However, it is clear that characteristic size and geometry of a sample play a part in the third condition of SB formulated above. Appearance of SB is also inverse proportional to the rate of absorbed dose.

4.3. Gauss approximation

Now we’ll try to specify parameters in (3a).

Let us suggest that density of radicals $n$ in volume $V_0$ chosen at random is distributed by Gaussian; after normalization we have:

$$p(n, V_0, \bar{n}, t) = \frac{1}{(V_0 \bar{n} \sqrt{2\pi \sigma}) \exp\left(-\frac{(n/\bar{n} - 1)^2}{2\sigma^2}\right)}$$  \hspace{1cm} (4).

The $\sigma$-quantity is a dimensionless mean square deviation. Value of $n_0$ can be evaluated from Jackson’s condition for uniform distribution of radicals:

$$n^{\text{crit}}_{CT} = \frac{0.62 \cdot C_m \cdot (T_{act} - T_0)}{x \cdot Q}$$  \hspace{1cm} (5),

where $x$ is the number of the nearest radical trap sites plus one (for the methane matrix, $x$ is 13); $C_m = C_p M$ is the molar specific heat; $Q$ is the heat of recombination per mole; $T_0$ is the irradiation temperature, and $n^{\text{crit}}_{CT} = n_0$. Jackson did not apply the Arrhenius law to the recombination rate, but only considered that a trapped radical is freed if $T \geq T_{act}$, and the free radical reacts at once with its neighbor if there is at least one.

Its estimate lays between 3 mol % and 4 mol % for solid methane. Now, the mean expectation time to burping at the instant $t$ may be expressed through only one unknown parameter $\sigma$, not including dimensional factors $T_0, \bar{D}_0,$ and $V_0$:

$$T_{SB} = \frac{(T_0 \bar{D}_0 V_0) \bar{n} \sigma \exp((n_0/\bar{n} - 1)^2/2\sigma^2)/(V \bar{D})}{C \bar{n} \sigma \exp((n_0/\bar{n} - 1)^2/2\sigma^2)/(V \bar{D})}$$  \hspace{1cm} (6).

Time dependence of $T_{SB}$ is hidden in $\bar{n}$.

Factor $C$ seems to be independent on size and geometry of a sample under irradiation, and on time of irradiation, except temperature: $C = f(T_0)$. Thus, we have an opportunity to make estimation of both $\sigma$-value and $C$-factor by comparing experimental values of mean expectation time to burping for different $\bar{n}$.

4.4. Estimation of parameters $C$ and $\sigma$ in (6)

a) Mean square deviation of density of radical.

First, it is required of the $\sigma$-value that the mean expectation time to burping $T_{SB}$ is rather weakly dependent on $\bar{n}$, at least, in the range of $\bar{n}$ typical for SB, that is, 0.5-0.8% for solid
methane and 0.7-1.5% for water ice [4,6,13]. Otherwise, no (or only small) dispersion in time of SB appearance would be observed in URAM-2 experiments. Really, SB in solid methane sample of URAM-2 experiments occurred once after 10 hours of irradiation but no burp occurred in three longer irradiations up to 26 hours. Dispersion of times to SB for water ice has similar character as it was already said in the introduction.

Now, basing on this requirement, it becomes possible to select value of $\sigma$. Thus, mean expectation time to burping is proportional to the complex

$$F(\bar{\bar{n}}, \sigma, n_0) = \bar{\bar{n}} \sigma \exp((n_0/\bar{\bar{n}} - 1)^2/2\sigma^2)$$

(7).

Calculated values of this complex, that is, relative value of mean expectation time to burping for a given sample, as function of $\bar{\bar{n}}$ for $n_0 = 3\%$ and for some values of $\sigma$ is shown in Table 1.

Table 1. Relative value of mean expectation time to burping, function (6).

<table>
<thead>
<tr>
<th>$\sigma^2$</th>
<th>$\bar{\bar{n}} = 0.4%$</th>
<th>$\bar{\bar{n}} = 0.5%$</th>
<th>$0.6%$</th>
<th>$0.75%$</th>
<th>$1.0%$</th>
<th>$1.25%$</th>
<th>$1.5%$</th>
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<tr>
<td>1</td>
<td>-</td>
<td>1.34 10$^7$</td>
<td>1788</td>
<td>67.5</td>
<td>7.39</td>
<td>3.33</td>
<td>2.47</td>
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<td>-</td>
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<td>152</td>
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<td>2.94</td>
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<td>-</td>
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<td>3.51</td>
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<td>5.8</td>
<td>3.37</td>
<td>3.00</td>
<td>3.07</td>
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<td>157</td>
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<td>8.87</td>
<td>4.62</td>
<td>3.3</td>
<td>3.19</td>
<td>3.40</td>
</tr>
</tbody>
</table>

Table 2. Probability of propagation of fast process of recombination beyond a cluster enriched with radicals and its inverse value, computer simulation.

<table>
<thead>
<tr>
<th>Mean density of radicals</th>
<th>$\bar{\bar{n}} = 0.4%$</th>
<th>$0.5%$</th>
<th>$0.6%$</th>
<th>$0.7%$</th>
<th>$0.8%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>0.01</td>
<td>0.04</td>
<td>0.18</td>
<td>0.4</td>
<td>0.65</td>
</tr>
<tr>
<td>1/p</td>
<td>100</td>
<td>25</td>
<td>5.55</td>
<td>2.5</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Spontaneous burps in water ice occurred in samples of 2.5-3 g mostly at $\bar{\bar{n}}$ between 0.7-1% after 8.4 hours in averaged, and one time – at 1.7-1.8% after 19 h for small sample of 0.4 g. Taking in mind that time of appearance of SB is inverse proportional to volume of a sample, it is easy to conclude that values of $\sigma^2$ from 2 to 3 satisfies almost equally experimental data for ice. As to the solid methane case, there is only one way to check which value of $\sigma$ is most adequate, namely: to compare situation at URAM-2 and IPNS solid methane moderators /14/. In URAM-2 there was one SB at $\bar{\bar{n}}$~0.8% after about 300 g-hours of total irradiation ("g-hours" means a product of irradiation time by mass of a sample) whereas IPNS moderators suffered from SB each 24-28 hours at $\bar{\bar{n}}$~0.5-0.6%. Taking in mind that space-averaged density of radicals for some time during initial period of each irradiation run is lower than limit for propagation of recombination wave through a sample (~0.4% for methane and ~0.6% for ice of water), one need to subtract this time from total time in order to receive expectation time to burping. After this operation we have about 150-200 g-hours for URAM-2 and 300-1000 g-hours for IPNS (ratio of mass of methane in URAM-2 to that of IPNS is about 1:100 and dose rate ratio is 5:1). Having relation (5) and Table 1, one may conclude that $\sigma^2$-value should be closer to 4 to have the best fit for all experimental data.
It is interesting to note that $\sigma^2 \sim 3 \pm 4$ was estimated by computer simulation of recoil proton tracks in 2D-geometry for radical distribution in the region of $\sim 10^{-3}$ cm [12]. With the same computer code, results of PC simulation for probability of propagation of fast process of recombination beyond the cluster of radicals of $10^{-4}$ cm was returned. Values which are inverse proportional to this evaluated probability, are placed in the Table 2 (below Table 1). Comparing the tables, it is easy to see that analytically evaluated variations of expectation time to burping with space-averaged density of radicals (Table 1, $\sigma^2 \approx 3 - 4$) is close to that for PC simulation in 2D geometry, Table 2, third row.

b) Evaluation of factor C.

Factor $C(T)$ for solid methane can be estimated also from experimental data of IPNS and URAM-2 project. Reciprocally compatible value of $C(T)$ was received to be between $300 \div 600$ [cm$^3$ h W/g] for $T=20-22$K. Temperature dependence is very small in the range 20-26K. For water ice, factor $C(T)$ appeared to be much less: $7.5-15$ at $T = 20-25$K. This fact is almost evident: due to very low heat capacity of ice (about 1/150 of heat capacity of methane at 30 K [15]) both parameters $n_0$ and $V_0$ are, most probably, less than those of methane. Weak dependence of probability of propagation of fast process of recombination beyond the burnable cluster of radicals on temperature of irradiation was checked by PC simulation in 2D-geometry. In Table 3 probability of propagation of fast process of recombination (in solid methane) is shown versus temperature of irradiation for given space-averaged density of radicals $\bar{n}=0.7\%$.

Table 3.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>20</th>
<th>22</th>
<th>24</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probability</td>
<td>0.23</td>
<td>0.40</td>
<td>0.63</td>
<td>0.72</td>
</tr>
</tbody>
</table>

4.5. SUMMARY AND CONCLUSION.

Finally, expression for the mean expectation time to burping at instant $t$ may be expressed as:

$$T_{SB} = C(T_{irr}) \bar{n}(t) \sigma \exp((n_0/\bar{n} - 1)^2/2\sigma^2)/(V \dot{D})$$  \hspace{1cm} (8),

where $C(T_{irr})$ is a factor depending on material of a moderator (strong dependence) and temperature of irradiation (weak dependence), $\bar{n}(t)$ is space-averaged density of radicals (mol. part), $\sigma$ is dimensionless mean square deviation of density of radical inside some small volume $V_0$ which size is not presented in an explicit form in (8), $n_0$ is the critical density of radicals uniformly distributed in small limited volume (evaluated, for example, by Jackson’s relation), and $V$ and $\dot{D}$ are volume of the sample and absorbed dose rate, respectively. It should be taking in mind, according to the three conditions for SB stated in the beginning, that total expectation time to SB is a sum of two values: $T_{SB}$ by (8) and time $T_0$ needed to accumulate radicals up to $\bar{n}_{crit}$-limit which can sustain propagation of recombination reaction through the sample as a whole.

$\bar{n}_{crit}$ is defined by size and shape of a sample, by its thermal properties, by cooling condition and by kinetics of radicals; evaluation of this value is not a subject of this probabilistic model. It is only worth to note that $\bar{n}_{crit} < n_0$. Really, less concentration of reagents is needed to sustain reaction which is already in action, than to initiate the process. Let us take an extreme
case: the sample of infinite size. Radicals of any low concentration will then react sooner or later: \( \tilde{n}_{\text{crit}} \approx 0 \); but, as higher concentration as sooner process of recombination begins). \( T_0 \) - value can be evaluated from the relation

\[ \tilde{n}_{\text{crit}} = R \tau (1 - \exp(-T_0/\tau)), \]

where \( \tau \) and \( R \) are “life time” of radicals and radical production rate, respectively. For low dose rate (and low value of \( R \) accordingly) and/or big volume of a sample, \( T_0 \) may prevail over \( T_{SB} \) resulting in deterministic character of SB appearance (if such is principally possible, that is, if \( \tilde{n}_{\text{crit}} < R \tau \)). \( T_0 \) will also prevail over \( T_{SB} \) for high dose rate and big volume of a sample, situation which is typical for cold moderators of advanced spallation neutron sources.

We understand that there are certain arbitrariness in the procedures used above. But it seems reasonable accounting for general conditionality of the model discussed. Function (1) is only one of many possible type of distribution of radicals in small volume of definite size chosen at random. Actually, type of the distribution is defined by many factors, such as structural defects, micro-cracks, crystallite interstitials, and diffusion of radicals which are quite unlikely to be analyzed with enough degree of certainty. This model may serve only for rough estimation of probability of spontaneous burping in solid methane and water ice until more rigorous theory is developed.

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Appendix
SYNTHETIC FREQUENCY SPECTRUM

\[ Z(\omega) = a_x Z_x(\omega) + a_y Z_y(\omega) + a_z Z_z(\omega) \]

A) Lattice modes

The dynamics of the solid lattice is represented by the Debye model:

\[ Z_i(\omega) = \frac{3 \omega^2}{\omega_i^3} \quad (\omega \leq \omega_i ; = 0 \text{ otherwise}) \]

\[ \Rightarrow \quad \gamma_i(0) = \frac{3}{\omega_i^3} \phi_i(\theta) \quad \Rightarrow \quad 2W_i = \frac{\hbar Q^2}{2M_i \omega_i} \cdot \frac{3}{\omega_i} \phi_i(\theta) \quad ; \quad M_i = M / \omega_i \]

B) Rotational modes

The `rotational band' is represented by:
\[ Z_0(\omega) = \omega^2 e^{-(\omega - \omega_0)^2 / 2\sigma^2} / K \]

a form that satisfies the required behaviour of the frequency distribution in the limit \( \omega \to 0 \).

\[ 2W_r = \frac{\hbar Q^2}{2M} \gamma(0) \quad ; \quad M = M / a_r \]

C) Vibrational modes

\textbf{Einstein model} to represent molecular vibrations:

\[ a_r Z_r(\omega) = \sum_j c_j \delta(\omega - \omega_j) \]

where \( \omega_j \) denotes the eigenfrequency of the \( j \)-th vibrational mode, and \( c_j \) its relative weight.

under the assumption that \( kT \ll \hbar \omega_j \forall j \Rightarrow n(\omega) = 0 \),

\[ \gamma_r(t) = \sum_j c_j \frac{\omega_j}{a_r} e^{i\omega_j t} \Rightarrow \gamma_r(0) = \sum_j c_j \frac{\omega_j}{a_r} \]

\[ \Rightarrow 2W_r = \frac{\hbar Q^2}{2} \sum_j \frac{\omega_j}{M_{r,j}} \]

with \( M_{r,j} = M / c_j \)

---

**METHANE HYDRATE**

- Produce optimized SFS for solid methane;
- Produce SMS for CH₄ in methane hydrate
- Perform MCNP calculations for
  - \textbf{ICE} at 112K (Inoue configuration)
  - \textbf{ICE, solCH₄, Clathrate} at 22K (Kiyanagi configuration)
Solid Methane
(~ 22K)
22 K

$\Phi(E)$ vs $E$ (meV)

- Meth NJOY
- Meth Synth
- Clath
- Ice
The Stern-Kirby-Durham Approach to ch₄-hydrate production

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Zentralabteilung Technologie
Forschungszentrum Jülich GmbH
52425 Jülich, Germany

Polycrystalline Methane Hydrate: Synthesis from Superheated Ice, and Low-Temperature Mechanical Properties

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Received September 8, 1997, Revised Manuscript Received November 17, 1997
Phase Diagram of the CH$_4$-H$_2$O system
Experimental Set up
Reaction Chamber for Hydrate Production

CH₄ (g) (at 35 MPa, 250 K)

1. CH₄ gas enters the chamber.
2. Granulated H₂O ice (180 - 250 μm grain size) is added.
3. Heat is applied to initiate hydrate formation.
4. Hydrate forms inside the chamber.

ethanol bath

thermocouple

ice

hydrate
Reaction Path

\[ \text{CH}_4 + 6\text{H}_2\text{O} \rightarrow \text{CH}_4 \cdot 6\text{H}_2\text{O} \]

Diagram showing the reaction path with pressure, CH\(_4\) (g), and temperature as variables. The diagram includes points labeled A, B, C, D, and E, with temperature and pressure changes indicated along the path. The text also mentions cooling and 100% methane hydrate.
Analysis: X-ray diffraction patterns

A
Methane hydrate, (as-molded)

B
post-deformation (run 368)

Intensity

2\theta, degrees
Comparison with non-hydrate forming gas:
Neon
Comparison with non-hydrate forming gas:

Neon

Morphology of clathrate surface during reaction
# Mechanical Tests: Conditions

## Table 1. Mechanical Test Conditions and Results

<table>
<thead>
<tr>
<th>run no.</th>
<th>step</th>
<th>$T$ (K)</th>
<th>$P_t$ (MPa)</th>
<th>$\dot{\varepsilon}$ (s$^{-1}$)</th>
<th>$\varepsilon_i$</th>
<th>$\sigma_i$ (MPa)</th>
<th>$\sigma_\infty$ (MPa)</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>281</td>
<td>1</td>
<td>160</td>
<td>50</td>
<td>$3.5 \times 10^{-4}$</td>
<td>0.125</td>
<td>&gt;85</td>
<td></td>
<td>strain hardening</td>
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<tr>
<td></td>
<td>2</td>
<td>160</td>
<td>50</td>
<td>$3.5 \times 10^{-7}$</td>
<td>0.150</td>
<td>60</td>
<td></td>
<td>strain hardening</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>160</td>
<td>50</td>
<td>$3.5 \times 10^{-4}$</td>
<td>0.160</td>
<td>100</td>
<td></td>
<td>brittle failure; $\approx$25% H$_2$O ice$^a$</td>
</tr>
<tr>
<td>282</td>
<td>1</td>
<td>140</td>
<td>50</td>
<td>$3.5 \times 10^{-4}$</td>
<td>0.160</td>
<td>71</td>
<td></td>
<td>failure, multiple events</td>
</tr>
<tr>
<td></td>
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<td>140</td>
<td>50</td>
<td>$3.5 \times 10^{-4}$</td>
<td>0.160</td>
<td>94</td>
<td></td>
<td>failure, multiple events; $\approx$25% ice$^b$</td>
</tr>
<tr>
<td>366</td>
<td>1</td>
<td>168</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pressurization and compaction only$^c$</td>
</tr>
<tr>
<td>367</td>
<td>1</td>
<td>185</td>
<td>100</td>
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<td>0.138</td>
<td>71</td>
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<td>strain hardening at $10^{-3}$ step</td>
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<tr>
<td></td>
<td>2</td>
<td>185</td>
<td>100</td>
<td>$3.5 \times 10^{-5}$</td>
<td>0.215</td>
<td>96</td>
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<td>$\approx$30% ice postdeformation</td>
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<tr>
<td>388</td>
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<td>$3.5 \times 10^{-3}$</td>
<td>0.185</td>
<td>102</td>
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<td>strain hardening; 25% ice$^b$</td>
</tr>
<tr>
<td>399</td>
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<td>168</td>
<td>100</td>
<td>$3.5 \times 10^{-3}$</td>
<td>0.16</td>
<td>100</td>
<td></td>
<td>identical run as 368$^d$</td>
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<td></td>
<td></td>
<td></td>
<td>no evolved CH$_4$ gas</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>1</td>
<td>200</td>
<td>$3.5 \times 10^{-3}$</td>
<td>0.120</td>
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<td>strain hardening at $10^{-3}$</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>no evolved gas$^{d,1}$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>200</td>
<td>100</td>
<td>$3.5 \times 10^{-3}$</td>
<td>0.230</td>
<td>85</td>
<td>80</td>
<td>$\approx$30% ice postdeformation</td>
</tr>
</tbody>
</table>
Mechanical Tests:
Apparatus
Mechanical Tests: Results

"Standard" H$_2$O ice
T = 160 K, P$_c$ = 50 MPa
\( \dot{\varepsilon} = 3.5 \times 10^{-5} \text{ s}^{-1} \)

Methane hydrate (run 368)
T = 168 K, P$_c$ = 100 MPa
\( \dot{\varepsilon} = 3.5 \times 10^{-5} \text{ s}^{-1} \)
Morphology of Indium Jacket

Figure 10. Indium jacket replicas of the surfaces of samples deformed within the ductile (A) and brittle (B) regimes. Compression direction is oriented vertically in both photographs. (A) Sample 357, deformed at 180 K, 100 MPa, and taken to 61% strain (Table 1). Oblique illumination highlights the surface topology and shows deformed grains standing in relief. Some of the plastically deformed hydride grains show pronounced elongation in the plane perpendicular to the direction of compression, presumably produced by dislocation creep. Many of the grains have grown significantly from their original size, likely by stress-induced coalescence of impinging grains within the compression plane. Fine-grained patches (such as those marked by arrows) are believed to be regions of precipitated ice (see text). (B) Sample 382, tested at 140 K and 50 MPa, that was taken to 18% strain and fractured during several events (Table 1). The individual grains and the void traces on the jacket stand out in relief. Grain sizes and sizes in the cold, brittle regime samples range equant and uniform at ~250 ± 50 μm.
Conclusion

- SKD approach is a viable solution for the production of clathrates
- single-phase material of high quality large volume, cohesive, polycrystalline aggregates with methane saturation, uniform grain size, random crystallographic orientation
- 29% porosity after reaction can be eliminated by pressurising
- no mechanical agitation is necessary during reaction
- reaction times ~ 8 h

Questions

- upscaling of experimental apparatus for 150 l clathrate/ day?
- reduction of exerted pressure by admixture of propane or other hydrocarbons?
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ACoM - 6

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