Enclosure 1. Tier-1 Application form – English version

APPLICATIONS ARE PREFERABLY DRAWN UP IN ENGLISH. AN ENGLISH TRANSLATION HAS TO BE ENCLOSED WITH APPLICATIONS SUBMITTED IN DUTCH.

The application form is available in English on the website

https://www.vscentrum.be/en/access-and-infrastructure/project-access-tier1

Title of the application:

Enhanced sampling study of the methylation of ethene, propene and trans-2-butene.

Name and first name of the applicant:

Bailleul Simon

Institution:

Ghent University

Research group / department:

Center for Molecular Modeling

Title / position:

PhD Fellow

e-mail address:

Simon.Bailleul@UGent.be

Total computing time that is needed, in node days:

3300

Total disk storage that is applied for (in GiB):

79.5 GB scratch space - 0.8 TB long-term storage (provided by UGent)

The total number of pages in this application should not exceed 17, excluding possible appendices (confirmation letter of financing institution, software license,…) which may be taken into account by the Tier-1 Allocation Board.

1. Title of the research project (with IWETO or FRIS link if available) within the framework of which computing time is applied for:

European Union's Horizon 2020 research and innovation programme (consolidator ERC grant agreement No 647755 – DYNPOR (2015-2020))

2. Describe your research project in short. Explicitly mention the scientific questions that you are planning to address and the overall scientific goals of the project. (max. 1 A4 in Arial 12):

In the last decades, significant progress has been made in the field of computational chemistry [1], making it possible for advanced molecular dynamics methods, which have the potential to model chemical reactions at operating conditions, to enter the scene. [2] Furthermore, for an optimal design of heterogeneous catalysts, a thorough understanding of elementary reaction steps on a molecular level is crucial. Solely based on experimental data, it has shown extremely challenging to gather such information due to the large number of reactions that take place simultaneously, which can be overcome by complementing the experimental information with theoretical simulations. [3] Therefore, the quest to attain chemical accuracy (4 kJ/mol for the energy barriers and one order of magnitude for the pre-exponential factors) using ab initio techniques is of utmost importance. A recent contribution to this quest is done by Piccini et al. [4] by presenting a divide-and-conquer strategy, enabling them to attain this chemical accuracy for the methylation of ethene, propene and trans-2-butene, key reaction steps in the methanol-to-olefin process. [2,3] With their results, they emphasize on the importance of accounting for the anharmonic behavior of the system. Therefore, we would like to simulate the same three reactions using advanced molecular dynamics, since these techniques are able to directly account for the dynamic behavior of the system. [2] In this way, the selected enhanced sampling technique can be benchmarked and its potential can be demonstrated. Thus, computationally quite expensive umbrella sampling [5] simulations of the methylation of ethene, propene and trans-2-butene will be performed in this Tier1-project to enable us to aid in the quest for chemical accuracy with ab initio simulations.

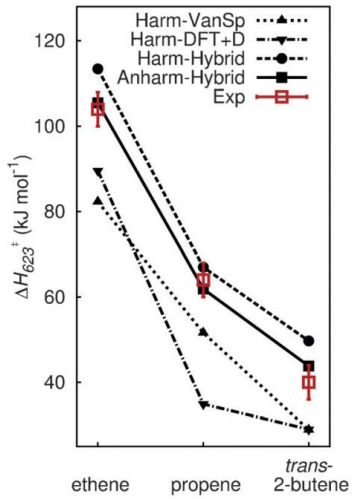

Figure 1: Calculated heats of activation at 623K for the methylation of ethene, propene and trans-2-butene, where Anharm-Hybrid represents the divide-and-conquer method proposed by Piccini et al. which attains chemical accuracy. [4]

[1] V. Van Speybroeck, K. Hemelsoet, L. Joos, M. Waroquier, R. G. Bell, C. R. A. Catlow, *Chem. Soc. Rev.* **2015**, *44*, 7044–7111.
[2] K. De Wispelaere, S. Bailleul, V. Van Speybroeck, *Catal. Sci. Technol.* **2016**, *6*, 2686–2705.
[3] V. Van Speybroeck, K. De Wispelaere, J. Van der Mynsbrugge, M. Vandichel, K. Hemelsoet, M. Waroquier, *Chem. Soc. Rev.* **2014**, *43*, 7326–7357.
[4] G. Piccini, M. Alessio, J. Sauer, *Angew. Chem. Int. Ed.* **2016**, *55*, 5235–5237.
[5] J. Kästner, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1*, 932–942.

3. Provide an engaging abstract (10 lines) for scientific communication on the website in layman's terms. Should this application be bound by a confidentiality agreement (see also item 12 of this application form), provide more details about the specific nature of the confidentiality and indicate why an abstract may not be published.

For optimal catalyst design, a thorough understanding of elementary reaction steps on a molecular level is crucial. Therefore, the quest to attain chemical accuracy (4 kJ/mol for the energy barriers and one order of magnitude for the pre-exponential factors) using ab initio techniques is of utmost importance. A recent contribution is done by Piccini et al. by presenting a divide-and-conquer strategy, emphasizing on the importance

of the anharmonic behavior of the system. Therefore, we would like to simulate the same reactions using umbrella sampling, since this technique is able to directly account for the dynamic behavior of the system enabling us to aid in the quest for chemical accuracy with ab initio simulations.

4. Financing institution or channel, financing the research project in full or in part (FWO, BOF, IWT, EU, ...): Please attach the confirmation letter as enclosure. In case the project has not gone through a scientific approval process attach a letter of approval of your own institute.

European Research Council under the European Union's Horizon 2020 research and innovation programme (consolidator ERC grant agreement No 647755 – DYNPOR (2015-2020))

The conformation letter is added in the Appendix.

5. Name and email address of the promoter(s) of the research project:

Prof. dr. ir. Veronique Van Speybroeck
Veronique.VanSpeybroeck@UGent.be

6. Persons mandated by the Applicant to compute on the Tier-1 within the framework of the present project: Please provide for every person:
   - name and first name
   - institution
   - research group / department
   - title / position
   - experience of using HPC resources in the past (Tier-0/Tier-1/Tier-2 infrastructure in Belgium and abroad)

Ir. Simon Bailleul – vsc41224
Ghent University, Center for Molecular Modeling
ERC PhD fellow
1 ½ year of experience with the Flemish TIER1 infrastructure
3 years of experience with TIER2 at Ghent University

Ir. Pieter Cnudde – vsc40920
Ghent University, Center for Molecular Modeling
PhD fellow
2 ½ years of experience with the Flemish TIER1 infrastructure

4 years of experience with TIER2 at Ghent University

Dr. ir. Kristof De Wispelaere – vsc40490
Ghent University, Center for Molecular Modeling
ERC Post-doc
3 ½ years of experience with the Flemish TIER1 infrastructure
½ year of experience with TIER1 and TIER2 in The Netherlands
6 ½ years of experience with TIER2 at Ghent University

Prof. dr. ir. Veronique Van Speybroeck – vsc40021
Ghent University, Center for Molecular Modeling
Full Professor
4 years of experience with the Flemish TIER1 infrastructure
8 ½ years of experience with TIER2 at Ghent University

7. Explain why this project needs to run on a Tier-1 system, why the machine you have requested is suitable for the project and how the use of the system will enable the science proposed (max. ½ A4 in Arial 12).

To perform all simulations proposed in this study, a computing time of over 3000 node days is needed to obtain accurate statistical averages from the umbrella sampling simulations. Running several multi-node jobs in parallel is imperative to complete this project in an acceptable timeframe. The ability to run a large number of jobs simultaneously on the Tier-1 infrastructure is therefore essential for the success of this research.

8. Justify the number of node days requested. This should include information such as: number and nature of computing tasks, software used, and the sequence in which they will be performed.
   Indicate for each typical computing task the required resources:

   - wall clock time (note that 3 days is the maximal wall clock time for any job;)
   - memory (maximum 128 GiB/node; 256 GiB/node is available upon motivated request)
   - number of nodes
   - number of CPU cores
   - disk space (estimated volume in GiB and the total number of files); make a clear distinction between usage of Tier-2 DATA/HOME partitions and the Tier-1 SCRATCH partition

- number of tasks, and an indication of how many such tasks would be submitted concurrently.

This information should take the form of a table (an example is provided as Table 1 on the next page). Provide additional descriptions of the computing tasks and comments as needed and clearly relate the described tasks to the tasks in the table. Resource estimates should be preferably based on the results of actual calculations on Tier-1 (via, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results and explain how you have calculated/rescaled the wall clock times, number of cores, etc.
(typically up to 2 A4 Arial 12).

During this study, three types of calculations will be performed using the CP2K software package on a periodic model of H-ZSM-5 consisting of 289 atoms and guest molecules with up to 18 atoms. The computational requirements for this study have been carefully considered based on test simulations on similar systems, performed on both the Tier-2 infrastructure at Ghent University (golett cluster) and the Tier-1 infrastructure at the University of Leuven. Based on the scaling tests (see item 10), we will perform multi-node jobs on **2 nodes**.

Calculation flow:

1. **Ab initio MD simulations (MD)**
   In a first step, ab initio molecular dynamics simulations are performed to study the nature, stability and dynamic interaction of the adsorbed hydrocarbon and methanol. Each simulation will be performed in the NPT ensemble at realistic reaction conditions, namely 623 K and 1 atm. A simulation length of **50 ps** is required to allow sufficient equilibration before the system will be biased in step 2 and step 3. MD simulations of comparable systems have shown that a 5 ps simulation requires approximately 4 node days on Tier-1 (Breniac). Therefore, it is expected that each of the 3 co-adsorbed alkene/methanol simulations will require **40 node days**.

2. **Creation of umbrellas**
   Next, different windows for umbrella sampling will be created along a predefined coordinate which is capable of unambiguously describing the studied methylation reaction. To create the windows, we drive the system from the reactants corresponding to adsorbed methanol and the alkene to the products, namely water and the methylated alkene, along the reaction coordinate in a metadynamics (MTD) simulation. Furthermore, the **MTD simulations** allow us to obtain a first estimate of the free energy profiles and methylation barriers. Simulations are carried out in the NVT ensemble at 623 K with a typical simulation length of 80 - 100 ps, depending on the height of the free energy barrier. Based on test simulations performed on the Tier-1 infrastructure (Breniac), Tier-2 infrastructure (golett cluster) and previous experience with MTD simulations on similar systems, each simulation is expected to take up approximately **60 node days**.
3. **Umbrella sampling (US)**
   To refine the free energy profile and cracking barrier estimates from the MTD simulations, umbrella sampling simulations are carried out on the **3 methylation reactions**. The reaction coordinate as identified in step 2 is divided in overlapping umbrella windows from the reactant to the product state. At least **25 equidistant windows** are required to reconstruct the free energy profile properly. For each of these 25 positions along the reaction coordinate, a 50 ps biased molecular dynamics simulation is needed to obtain a converged free energy profile. The simulations will again run in the NVT ensemble at 623 K, thus requiring **40 node days** per window. The 25 MD simulations for each reaction can be easily run in parallel with respect to each other to reduce the wall time for this type of simulations.

Table 1 summarizes the estimated node and core days for each simulation type.

Table 1. Estimated core and node days for each simulation type.

Job type	# of simulations	Node days per simulation	Total node days	Total core days
MD	3	40 (= 20 days x 2 nodes)	120	3360
MTD	3	60 (= 30 days x 2 nodes)	180	5040
US	3 x 25	40 (= 20 days x 2 nodes)	3000	84000
			3300	**92400**

Table 2 summarizes the requirements for scratch space and long-term storage for each simulation type. Because of the long simulation times, a complete MD trajectory cannot be obtained within the wall time limit of 72 hours, but requires several restarts. As a result, the scratch volume per simulation is relatively low.

Table 2. Estimated scratch space and long-term storage for each simulation type.

Job type	Scratch [GB/run]	Long term storage [GB/run]	Total scratch [GB]	Total long term storage [GB]
MD	0.5	3.5	3 x 0.5 = 1.5	3 x 3.5 = 10.5
MTD	1	10	3 x 1 = 3	3 x 10 = 30
US	1	10	75 x 1 = 75	75 x 10 = 750
			79.5	**790.5**

9. Describe the software required to perform the computing task(s). Please clearly provide the following per item in this regard:

   - a reference to the software's web page
   - the software license system (open source, GPL, etc.)
   - if there is no free academic use of the software, state which license makes the installation and the use valid on the Tier-1 by the Applicant (+ add a copy of the signed license)

- if need be, which license server will be used (name + IP address)
- whether the software is already available on the Tier-1 and, if this is not the case, compilation and installation instructions (possibly with reference to existing Tier-2 installation)

Molecular dynamics simulations and umbrella sampling will be performed using the CP2K software package (http://www.cp2k.org/) with the PLUMED code (http://www.plumed.org), which are both freely available under the GPL license. The required version of the program (CP2K/3.0-intel-2016a-PLUMED-2.2.1-impi-5.1.2.150) is already available on Tier-1.

Provide the results of scaling tests that were conducted with this software, preferably on the current VSC Tier-1 (using, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not run on the current VSC Tier-1, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results and how you think this compares to the current VSC Tier-1. If a different system/problem size is used provide some guidance how it relates to the problem size in the application.
Provide both a table and scaling plot such as table 2 and plot 1 below (typically up to 3 A4 in Arial 12).

A scaling test for the CP2K software package (version CP2K/3.0-intel-2016a) on TIER1 (Breniac) has been conducted using a model system similar to the systems under study, namely a 2-hexene molecule adsorbed in H-ZSM-5. Short NVT simulations (2000 steps) have been performed on 28, 56, 112, 224 and 448 cores of the Tier-1 cluster. The results of the scaling test are summarized in Table 3. In Figure 2, the speedup normalized to the 28 core simulation is plotted for the short scaling test MD simulations. This graph indicates that optimal scaling is achieved up to 2 nodes.

Table 3. Summary of the scaling test of a 2000 steps MD simulation on a 2-hexene molecule adsorbed in a H-ZSM-5 unit cell.

# nodes	# cores	Wall clock time (s)	Speedup	Efficiency
1	28	29952	1.00	1.00
2	56	16044	1.87	0.93
4	112	10164	2.95	0.74
8	224	6522	4.60	0.57
16	448	5286	5.67	0.35

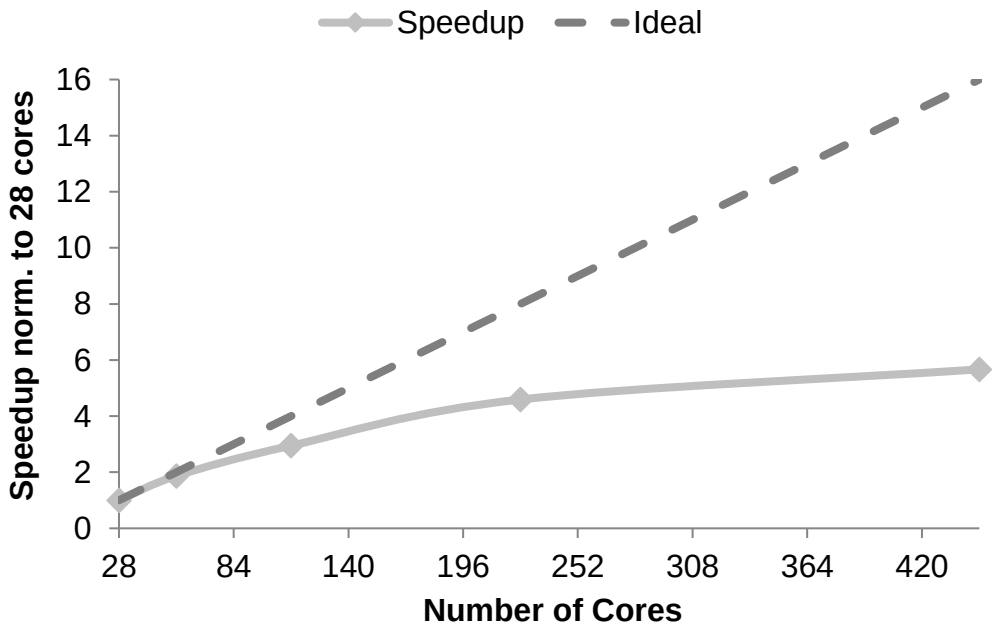

Figure 2. Speedup normalized to 28 cores for an ab initio MD simulation on a 2-hexene molecule adsorbed in H-ZSM-5 as a model system using the CP2K software package.

10. Describe how you will manage the resources requested in the period during which the task is to be performed. What usage pattern do you anticipate (similar usage on monthly basis, bursts,

…)? Provide a data management plan (transfer of files to/from Tier1).

We estimate that the proposed simulations can be completed over a time period of approximately 6 months. Similar usage on a monthly basis is expected. For each of the 3 reactions under investigation, first an MD and MTD simulation will be performed. Hereafter, the 25 US simulations are calculated in parallel. The 3 reactions will be studied in parallel which will take 6 months to complete. This estimated timeframe takes into account the actual runtime of the simulations, as well as intermediate data analysis tasks and frequent job restarts.

Since each simulation (MD, MTD and US) cannot be completed within the wall time of 72 hours, several job restarts are required. For each run, a maximum of 500Mb of scratch space is required. After 72 hours, all data is automatically transferred to the Tier2 scratch storage and the Tier1 scratch space is cleared again before the job is restarted. Consequently, scratch volume per simulation is relatively low and the load on the Tier1 scratch will be minimal. Moreover, the data transfer is thus spread equally over the duration of the project. The data transfer of the input files at the start of the job is negligible (approximately 300KB).

11. List the granted computing time allocations to the promoter(s) of this research project, on the Flemish Tier-1 systems, as well as other Tier-1 and Tier-0 systems. Also, describe the scientific output obtained within the framework of computing time that was granted during the past two years on the Flemish Tier-1 systems or on other Tier-1 or Tier-0 supercomputers. DOI links are sufficient.

List of granted research projects of the Flemish TIER1 system:

- Dynamical kinetic study of zeolite catalyzed reactions (K. De Wispelaere, 4371 node days, 07/07/2014 – 31/12/2014)
- Exploring the kinetics and selectivity of butene cracking using molecular dynamics simulations (J. Van der Mynsbrugge, 4864 node days, 01/01/2015 – 30/06/2015)
- Characterizing adsorption properties of C4 – C6 alkenes on H-ZSM-5 using molecular dynamics simulations (P. Cnudde, 4260 node days, 13/07/2015 – 31/12/2015)

- Dynamical first principle benchmark studies on alkene methylation in H-ZSM-5 (K. De Wispelaere, 1400 node days, 01/12/2015 – 30/06/2016)
- Ab initio molecular dynamics study on the role of water in the reaction mechanism during methanol conversion in H-SAPO-34 (S. Bailleul, 4880 node days, 01/03/2016 – 31/08/2016)
- DFT study of reaction paths in zeolite-catalyzed 2-hexene cracking (P. Cnudde, 4536 node days, 15/08/2016 – 31/12/2016)
- Dynamical first principle modelling of zeolite dealumination in H-SSZ-13 (K. De Wispelaere, 3624 node days, 01/07/2016 – 31/10/2016)
- Benchmark study of ab initio molecular dynamics simulations for the methylation of HMB (S. Bailleul, 4812 node days, 1/11/2016 – 30/04/2017)
- Ab initio study on the stability of cracking intermediates (P. Cnudde, 4920 node days, 03/07/2017 – 03/01/2018)

List of scientific output within the framework of granted computing time:

- http://dx.doi.org/10.1016/j.jcat.2017.03.007
- http://dx.doi.org/10.1016/j.jcat.2016.11.010
- http://dx.doi.org/10.1016/j.jcat.2016.05.018
- http://dx.doi.org/10.1002/cctc.201600650
- http://dx.doi.org/10.1039/C5CY02073E
- http://dx.doi.org/10.1021/acscatal.5b02139
- http://dx.doi.org/10.1002/chem.201500473
- http://dx.doi.org/10.1016/j.jcat.2015.01.013

12. Are the applicants of this application bound by a confidentiality agreement? If so, the abstract of this application will not be published on the website of the FWO / Flemish Supercomputer Center, only the title.

No

Appendix: Conformation letter

Ref. Ares(2015)644832 - 16/02/2015

European Research Council
Executive Agency

Established by the European Commission

Brussels,

Veronique VAN SPEYBROECK
UNIVERSITEIT GENT
Technologiepark 903
9052 ZWIJNAARDE
BELGIUM

Subject: Invitation to grant preparation
H2020 - ERC-2014-CoG
647755 - DYNPOR

Dear **Veronique VAN SPEYBROECK**,

We are pleased to inform you that the European Research Council Executive Agency (ERCEA) is now in a position to initiate the preparation of the grant agreement for your abovementioned proposal.

The ERCEA intends to follow the Evaluation Report advice which has been already transmitted to you and consequently, it is estimated that the maximum EU financial contribution to your project could be up to 1 993 750.00 Euro for a period of up to 60 months.

With reference to the submitted proposal and its evaluation, the grant preparation shall be based on the following:

The deadline for the submission of the data required for the grant agreement, including any additional documents, as detailed in the Annex attached is 02/03/2015.

Failure to respect the deadline indicated above will be considered as a wish not to enter into the grant preparation and, therefore, to withdraw your proposal. In such a case, the ERCEA will initiate the procedures to reject your proposal, unless alternative arrangements have been accepted by the ERCEA.

Considering the above, we expect the granting process to be completed as soon as possible, and within 4 weeks of the date of this letter.

The grant preparation process, including communication with the **ERCEA**, and the subsequent signature of the Grant Agreement, shall be carried out through the Research **Participant Portal Grant Management Service** (PP GMS). By logging into your individual account in the Participant Portal and selecting the project under the Grant Management Service section, each step of the grant preparation process can be followed, and all relevant documents consulted, at any time.

European Commission | Horizon 2020 European Union funding for Research & Innovation

ERC Executive Agency – Grant Management Department
BE-1049 Brussels, Belgium | http://erc.europa.eu | Email: ERC-COG-GRANTING@ec.europa.eu

Please see however in the Annex of this letter the additional documents required which you will have to submit by email to the officer in charge of your project (see: "Additional Information for the grant preparation attached to this invitation").

The Grant Agreement preparation data provided through the Participant Portal (pre-filled with the information already available in the Beneficiary Register, and structured data from your proposal) are needed in order to prepare the grant agreement and provide programme-wide statistical information.

Kindly note that some information related to the legal and financial status of participants is read-only and may only be updated by the Legal Entity Appointed Representative (LEAR) of the organisations concerned through the Participant Portal http://ec.europa.eu/research/participants/portal. It is therefore important to ensure that all participants are aware of the need to appoint a **LEAR, within 2 weeks from the date of dispatch of this invitation letter**.

Further information providing practical details on grant preparation as well as technical guidance, are available in the H2020 Online Manual section of the Participant Portal.

This letter should not be regarded under any circumstances as a formal commitment by the ERCEA to provide financial support, as this depends on the satisfactory and timely conclusion of grant agreement preparation and on the satisfactory finalisation of the ethics review process (where applicable).

In case your project needs to undergo an ethics review and/or assessment by the ERCEA, you will, if not already the case, be soon contacted by our Scientific Department (Ethics team). We draw your attention to the fact that the granting process cannot be finalised and your project can not start until all ethical issues are either cleared or have been considered by the Ethics team as having to be cleared during the course of the project.

Should you need further details concerning the granting process, you are invited to contact the **officer in charge of your project** (Mr. Kris PIOT – functional e-mail address ERC-COG-GRANTING@ec.europa.eu)

Yours sincerely,

Marja HENNESSY
Head of Unit
ERC Executive Agency

Enclosure(s):
Annex: Additional Information for the grant preparation

cc: Nathalie Vandepitte

European Commission | Horizon 2020 European Union Funding for Research & Innovation
ERC Executive Agency – Grant Management Department
BE-1049 Brussels, Belgium | http://erc.europa.eu | Email: ERC-COG-GRANTING@ec.europa.eu

Annex: Additional Information for the grant preparation

Please remember that Horizon 2020 actions (i.e. projects) must be implemented in accordance with the assessed proposal. The Description of the Action must not differ from the proposal (see also below). This is without prejudice to any corrections needed:

- as a result of an ethical review,
- to ensure the project conforms to the applicable rules, e.g. legal and financial rules,
- to remove clerical errors or clear inconsistencies,
- when, under exceptional circumstances, a participant is removed during grant preparation.

In line with the above, the following should be taken into account for the ERC grant agreement preparation:

1. Description of the Action (DoA, Annex 1 to the grant agreement) and Estimated budget for the action (Annex 2)

The **Description of the Action** (DoA, Annex 1 to the grant agreement) should include the narrative description of the budget, as in the proposal. The budget table should only be shown in the **Estimated budget** for the action (Annex 2).

Therefore, when preparing it, please remember to **remove the budget table** from your proposal (Part B), before uploading the Description of the Action (DoA) in the Participant portal. However tables that provide additional information (e.g. more detailed breakdown of certain cost categories) compared to the budget table of Annex 2 can remain. **All eligible costs must be included in the narrative budget description of the DoA.** Please remember to use whole Euro values only.

Description of the Action (Annex 1) – **Part A**: please note that section 1.3. Workplan Tables - Detailed implementation does not have to be filled in for the ERC grant preparation.

2. Statement of Changes (SoC)

In addition to the submission of the data through the system please also provide a one page statement describing any changes that have been made in the Description of the Action compared to the original proposal.
Even in case there are no changes in the DoA from the original proposal, **please include a clear statement** ("Statement of changes", to be uploaded in the Participant portal).

3. Supplementary Agreement (SA)

Please use the model for H2020 ERC supplementary agreement found at the ERC Documents website (***to be sent by email to the officer in charge of your project***).

4. PI's passport

Only if the PI has **not** provided a copy of his/her identity document during the interview (evaluation of proposal) **or** this document has been modified or renewed, then the PI is requested to provide a copy of such a document (***to be sent by email to the officer in charge of your project***).

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5. Links to other useful documents and guidelines:

Participant Portal

Proposal Management and Grant Preparation

Grant Preparation

Grant signature

Should you have any questions or encounter any difficulties during the electronic submission of an Application, please contact by e-mail:
Associatie KU Leuven: hpcinfo@kuleuven.be
Associatie Universiteit Gent: hpc@ugent.be
Associatie Universiteit Hogescholen Antwerpen: hpc@uantwerpen.be
Associatie Universiteit Hogescholen Limburg: geertjan.bex@uhasselt.be
Universitaire Associatie Brussel: hpc@vub.ac.be
For the other institutions: caroline.volckaert@FWO.be