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Theory and modelling: general discussion

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Deanna M. D'Alessandro opened a general discussion of the paper by François-Xavier Coudert: What is the potential for your high-throughput screening methodology to obtain information on the dynamics and kinetics of separation processes such as Xe/Kr separation?

François-Xavier Coudert answered: The thermodynamics of adsorption has been the topic of many more high-throughput studies than the transport of the adsorbed molecules, in good part because it is easier to study at this scale. Brute-force molecular dynamics simulations of guest diffusion are very expensive in terms of computational time, especially if one is interested in transport outside of the "zero loading" limit.

Alternative approaches have been proposed, such as a multi-scale screening workflow combining molecular dynamics with nudged elastic band characterisation of classical energy barriers, to screen MOFs for kinetic separation of propane and propene.[1] This still requires strong pre-screening in order to limit the number of systems that have to be directly simulated.

Another recent advance in this area is a study by Mace *et al.*[2] that is proposing an alternative multiscale approach, by computing hopping rates between adsorption sites using transition state theory (based on a statistical analysis of the potential energy surface inside the nanopores) and using that information as input into a kinetic Monte Carlo simulation. I believe this method shows great potential.

[1] Y. Pramudya, S. Bonakala, D. Antypov, P. M. Bhatt, A. Shkurenko, M. Eddaoudi, M. J. Rosseinsky and M. S. Dyer, *Phys. Chem. Chem. Phys.*, 2020, **22**, 23073–23082.
[2] A. Mace, S. Barthel and B. Smit, *J. Chem. Theory Comput.*, 2019, **15**(4), 2127–2141.

Dmytro Antypov asked: When the MOF structures were selected for the high-throughput calculations, were the pore limiting diameter and cavity diameter of each MOF considered to assess whether the guest molecules can respectively diffuse through and reside in the pore?

More generally, what are your thoughts on taking the framework flexibility into account in the simulations of thermodynamic properties?

François-Xavier Coudert responded: There is a general expectation that flexibility in nanoporous materials is not crucial to take into account in order to predict thermodynamic properties. This appears to be true in general at low loading, but may not hold at high guest uptake, as demonstrated in ref. 1.

More importantly, framework flexibility may drastically impact transport properties such as diffusion coefficients. It has certainly been shown in several studies in the past that ZIF frameworks, for example, can let molecules diffuse that would appear to be blocked by narrow windows based on geometric considerations.[2]

In the current state of things, including framework flexibility in high-throughput screening workflows is limited by the need for an accurate intramolecular force field for the flexible material. Recent advances in the systematic development of force fields based on *ab initio* data[3,4] may get us closer to that ultimate goal.

1 M. Agrawal and D. S. Sholl, *ACS Appl. Mater. Interfaces*, 2019, **11**(34), 31060–31068.
2 C. Han, Y. Yang and D. S. Sholl, *J. Phys. Chem. C*, 2020, **124**(37), 20203–20212.
3 J. P. Dürholt, G. Fraux, F.-X. Coudert and R. Schmid, *J. Chem. Theory Comput.*, 2019, **15**(4), 2420–2432.
4 L. Vanduyfhuys, S. Vandenbrande, J. Wieme, M. Waroquier, T. Verstraelen and V. Van Speybroeck, *J. Comp. Chem.*, 2018, **39**(16), 999–1011.

Michael Zaworotko commented: My question concerns the reliability of modelling when sorbent–sorbate interactions are strong. Based upon my experience in collaborations with theoreticians (>40 papers), there is high reliability on the determination of loading and structure of binding sites, but energies tend to disagree with experimental data, typically on the low side. H-bonding and polarisability, especially induced polarisation, can affect energetics calculations. Is this a general challenge for modelling? Is water a particular challenge or is it no different to CO_2 or methane?

François-Xavier Coudert responded: Water is a tricky system to model even in the bulk phase, and especially so when confined in nanopores. Classical models tend to be inaccurate at capturing the details of the sorbent–sorbate interactions when the sorbate is highly polar, and water is probably the usual worst case – for the reasons you listed.

One possible solution is the use of more advanced classical models, such as many-body potentials, used with success by the group of Francesco Paesani.[1] They have, as an example, recently shown that it can describe in detail the hydrogen bonding pattern of confined water in a MOF with open metal sites.[2]

Another possibility is to describe water–water and water–host interactions at the quantum chemical level, with DFT. We have found in the past – studying water adsorption in flexible nanoporous materials – that it performs particularly well there, combining an accurate representation of the water–host interactions with that of the many soft degrees of freedom of the material itself. Therefore, it can describe not only the structure of the confined phase,[3] but also its energetics and its balance with the energetics of the host framework.[4]

1 F. Paesani, *Acc. Chem. Res.*, 2016, **49**(9), 1844–1851.
2 A. J. Rieth, K. M. Hunter, M. Dincă and F. Paesani, *Nat. Comm.*, 2019, **10**, 4771.

3 V. Haigis, F.-X. Coudert, R. Vuilleumiera and A. Boutin, *Phys. Chem. Chem. Phys.*, 2013, **15**, 19049–19056.

4 F.-X. Coudert, A. U. Ortiz, V. Haigis, D. Bousquet, A. H. Fuchs, A. Ballandras, G. Weber, I. Bezverkhyy, N. Geoffroy, J.-P. Bellat, G. Ortiz, G. Chaplais, J. Patarin and A. Boutin, *J. Phys. Chem. C*, 2014, **118**(10), 5397–5405.

Matthias Vandichel queried: Following on from Prof. Michael Zaworotko's question. In air, we can imagine that at a certain relative humidity, there will be a distribution of water molecules in different configurations (*e.g.* monomer, dimer, trimer, …). Do you think that GCMC methodologies should also consider adsorption of such a distribution of multimeric water species to predict water adsorption isotherms better? For some MOF-materials, we have observed that if we consider adsorption of a water dimer, this results in a better prediction of the water adsorption isotherm than the standard approach with monomeric water. Do you think such GCMC methodology can be more generally implemented?

François-Xavier Coudert explained: Once the equilibrium is reached, GCMC simulations will sample the configuration space of the water molecules adsorbed inside the pores, including all possible intermolecular arrangements (monomers, dimers, trimers, *etc.*), without the need for explicit modelling of these arrangements. Because the dimeric state, for example, can be achieved by inserting two molecules one after another, the description of water molecules as individual entities fully represents the configuration space.

In practice, however, when dealing with GCMC simulations of condensed phases such as the confined liquid, reaching this equilibrium can be difficult and biased MC moves can be used in order to speed things up. I suppose it is possible to consider direct insertion of dimers, for example, as long as the generation probability, acceptance probability, and probabilities of the reverse move are designed to maintain detailed balance. This would be, in a way, similar to pre-insertion biased moves or configurational bias Monte Carlo for flexible molecules.[1] It may speed up convergence, but it should not change the prediction of adsorption isotherms (or the structural properties of confined water) in a well-equilibrated simulation.

1 J. I. Siepmann and D. Frenkel, *Mol. Phys.*, 1992, **75**(1), 59–70.

Matthias Vandichel commented: There is a poster presentation by Amin Koochaki on this.[1] Potentially, if we have condensation at the outer surface of the MOF-materials, then the distribution of water molecules close to the pore will be also more multimeric in nature. So, that will automatically affect whether for example water as a monomer gets adsorbed or water as a dimer. So the condensation phenomenon is very important and certainly also for the kinetics of water sorption.

1 https://epostersonline.com/mofsfd2021/node/108.

François-Xavier Coudert communicated in reply: The distribution of water structure at the interface has no direct consequence on the distribution of water structure inside the material, if the two phases are in thermodynamic equilibrium. I think that the more important effect of outer surface adsorption would be, as you point out, on the adsorption kinetics and water transport.

For GCMC, I am not aware of this being done for water, however, it is something that is done a lot for the adsorption of flexible molecules. Because if you are looking for example at *n*-octane adsorption, then you have the question of all possible configurations. You cannot insert the molecule in only one of its conformations. You have to take into account all the conformations possible. In a way, it is the same for water. It has a complex coordination state and you want to account for that. So, in theory, it is possible. It should also be possible to do concerted insertion move or biased insertion move which would in the end account to the same thing. In most of the systems I know, the limitation for the reliability and the accuracy of the prediction is not the GCMC itself, it is the underlying models for the potential energy surface and the interactions. It is possible that there are some unusual cases. Actually, if you can send me that reference when it is published, I am interested. I think it would be more an exception than the rule in my gut feeling.

Matthias Vandichel further commented: Thanks for your response. Suppose water condensation is happening at the outer surface of the MOF materials, then the distribution of water molecules at the surface, close to the MOF-pores, will also be more multimeric in nature, more similar to a liquid water phase. Therefore, if the adsorption isotherm is theoretically predicted with GCMC, it might still be important to consider the initial distribution of water molecules in different configurations (*e.g.* monomer, dimer, trimer, …) prior to adsorption. On the other hand, a hydrated film layer onto a MOF-surface will result in a concentration (activity) gradient between the film and the humid gas phase with specific relative humidity (%-RH). Therefore, hydrated film forming processes and condensation provide the driving force and will be an important factor in the kinetics of water sorption. By tailoring the MOF-outer surface, the water sorption kinetics can potentially be further improved.

François-Xavier Coudert said: It is true that phenomena occurring at the external surface are still quite a mystery in most cases. I would argue that the details of the external surfaces are not very well known.

Qiaowei Li opened a general discussion of the paper by Mikhail Suyetin: Could defects in MOFs play a big role in adsorption capacity? Could descriptors for defects be incorporated into the model?

Mikhail Suyetin answered: Yes, defects can affect adsorption capacity.

These defects are indirectly represented in descriptors. Defects change the surface area, pore volume, and density. By having a set of MOFs you are training the model to behave in a particular way. Then if you are going to study a similar, but new MOF, you will get a nice result. and, of course there is another approach, you can directly add new variables to the equation for describing defects.

Isabel Cooley remarked: The three descriptors you have used seem to perform well, how did you choose them, and do you think the same three descriptors would perform similarly well for other MOF/gas systems? Also, in the paper you mention that you tried using six descriptors and didn't see any better fitting than with the three. What were the other descriptors you considered?

Mikhail Suyetin answered: Surface area, pore volume and density are fundamental parameters of porous materials, *i.e.* descriptors. I have no idea about application for other MOF/gas systems. I did not try. About the other descriptors – please read the paper. They are all mentioned there.

Vonika Ka-Man Au commented: It is fascinating to see that only three descriptors can predict the methane uptake properties accurately.

As the descriptors are all crystal parameters, how can they account for the surface properties of the MOFs, such as the effects of surface functional groups, hydrophobicity/hydrophilicity and so on?

Mikhail Suyetin responded: Thank you for the question. These effects are indirectly represented in the descriptors. It is obvious, if you are adding a functional group to a MOF, you are changing the surface area, pore volume, and density. Having a set of MOFs means you are training the model to behave in a particular way. Then if you are going to study a similar, but new MOF, you will get a nice result.

Sihai Yang continued the discussion of the paper by François-Xavier Coudert: Can state of the art modelling of gas adsorption in porous MOF consider the cleavage or construction of chemical bonds?

François-Xavier Coudert replied: High-throughput modelling is based on Grand Canonical Monte Carlo simulations, which is most commonly performed by considering a classical approximation (force field) of the host–guest interactions. Such an approximation does not describe reactivity, *i.e.*, the breaking and formation of chemical bonds.

Ab initio molecular dynamics, on the other hand, can accurately describe chemical phenomena, and chemisorption in particular. Such methods have been used in the literature to study, for example: the cooperative insertion of CO_2 in diamine-appended MOFs;[1] water-induced structural transitions, involving bond rearrangement;[2] and the hydrothermal stability of supramolecular materials, where water can disrupt the framework coordination.[3]

Finally, I note that while Monte Carlo methods can be coupled with an *ab initio* evaluation of the potential energy surface (for example, see ref. 4), this is in practice too expensive for practical uses in the field of adsorption, and especially in the context of high-throughput studies.

1 T. McDonald, J. Mason, X. Kong *et al.*, *Nature*, 2015, **519**, 303–308.

2 S. Tominaka, F.-X. Coudert, T. D. Dao, T. Nagao and A. K. Cheetham, *J. Am. Chem. Soc.*, 2015, **137**(20), 6428–6431.

3 V. Haigis, F.-X. Coudert, R. Vuilleumier, A. Boutin and A. H. Fuchs, *J. Phys. Chem. Lett.*, 2015, **6**(21), 4365–4370.

4 M. J. McGrath, J. I. Siepmann, I.-F. W. Kuo, C. J. Mundy, J. VandeVondele, J. Hutter, F. Mohamed and M. Krack, *ChemPhysChem*, 2005, **6**(9), 1894–1901.

Mikhail Suyetin added: DFT simulations can do it, but it is computationally expensive. Another approach is to use so-called reactive force-fields. They are much faster than DFT.

Sihai Yang addressed François-Xavier Coudert and Mikhail Suyetin: How many MOFs are there in the world?

Mikhail Suyetin responded: This is out of my expertise. Nowdays every MOFs' theoretical group is designing a database with thousands and thousands of MOFs.

François-Xavier Coudert replied: Many more than people usually assume! This is a common question, often asked at conferences and on social media.[1] In answer, the number of MOFs usually quoted comes from estimates from databases. Depending on how one characterises MOFs, the CCDC says[2] that its database contains more than 100 000 MOF-like frameworks (*i.e.*, coordination polymers), of which the CSD MOF collection extracts 10 636 3D porous MOFs.[3] However, answers based on crystalline databases neglect a lot of possible materials, either with amorphous structures, or crystals whose structure could not be determined for a variety of reasons. There are many more MOFs out there, including samples never fully characterised in someone's drawer.

[1] Twitter, 19 March 2021, https://twitter.com/keene_chemistry/status/1373043608547393540.
[2] CCDC, How many MOFs are there in the CSD?, https://www.ccdc.cam.ac.uk/support-and-resources/support/case/?caseid=9833bd2c-27f9-4ff7-8186-71a9b415f012.
[3] CSD MOF Collection, https://www.ccdc.cam.ac.uk/Community/csd-community/csd-mof-collection/.

Qiaowei Li continued the discussion of the paper by Mikhail Suyetin: Is there a bigger challenge for predicting gas adsorption properties of multivariate MOFs or MOF glasses compared to single component MOFs?

Mikhail Suyetin replied: No. I believe, this question was discussed already during a session with myself and Prof. François-Xavier Coudert. A conventional GCMC approach can be applied to obtain isotherms.

François-Xavier Coudert answered: Multivariate MOFs, with multiple ligands or multiple metals, can be more difficult to predict than "simple" materials. Metals are generally (but not always!) assumed to be distributed randomly in the structure, and therefore the impact on adsorption properties is that of a "mean field", that can be easily described by the same approaches as single-metal MOFs. For MOFs with multiple ligands, however, the distribution of the different linkers can play a key role in the properties of the MOF, including adsorption and mechanical properties (see, for example, ref. 1). This can lead to difficulties in the accurate modeling of adsorption properties, especially in a high-throughput context.

When it comes to MOF glasses, the difficulty is not in the prediction of adsorption properties from a given model of the amorphous structure, but in the generation of that disordered model in the first place. Therefore, the key point is the generation of the glass model (for example, by Reverse Monte Carlo, see ref. 2), which will be crucial for the accurate calculation of gas adsorption.

1 S. J. Lee, C. Doussot, A. Baux, L. Liu, G. B. Jameson, C. Richardson, J. J. Pak, F. Trousselet, F.-X. Coudert and S. G. Telfer, *Chem. Mater.*, 2016, **28**(1), 368–375.
2 T. D. Bennett, A. L. Goodwin, M. T. Dove, D. A. Keen, M. G. Tucker, E. R. Barney, A. K. Soper, E. G. Bithell, J.-C. Tan and A. K. Cheetham, *Phys. Rev. Lett.*, **104**, 115503.

Martin Schroder opened a general discussion of the paper by Elena Besley†: What features and functional groups in a MOF enable the selective capture of H_2S?

Elena Besley responded: The removal of the environmentally toxic and corrosive acid gases such as hydrogen sulfide (H_2S) from gas mixtures is a long-standing industrial challenge. A good approach is to look for MOFs structures in which high oxidation state metal ions are combined with carboxylate linkers to generate strong bonds resistant to chemical attack. H_2S can be also eliminated in an acid - base reaction by modifying MOFs structure with amines in order to improve H_2S uptake by taking advantage of available nitrogen sites and high affinity for acid gases. It is important, however, that by doing so we do not block the internal pores and surface of the modified MOF. Generally, functionalisation of the MOF's surface can results in the increased uptake of H_2S. Fluorinated linkers, as for example in MIL-101(Cr)-4F(1%), showed good promised for enhanced H_2S capture.

H_2S tends to form a strong and often irreversible metal–sulfur bond, which can cleave other coordination bonds between the metal centres and linkers, leading to disintegration of MOF structure. MOFs with open metal sites, such as HKUST-1, IRMOF-3, MIL-53(Fe), disintegrate readily upon the uptake of H_2S molecule, forming metal sulfides. In the presence of water, the structural degradation of MOF can accelerate even further due to the formation of additional acidic species. A very small amount of H_2O compromises the stability of HKUST-1 since the metal-coordinated linkers are replaced by H_2O or OH^-. In this regard, water – stable MOFs with strong coordination bonds between metal nodes and organic linker, such as MIL-101 family, ZIFs, and zirconium-based carboxylates, can be used for desulfurisation in the presence of water. A reversible process following successful capture of H_2S can be also achieved through weaker non-covalent interactions between H_2S and the functionalised linkers, such as hydrogen bonds or donor – acceptor bonds with the uncoordinated metal sites.

In our paper, we focus predominantly on hydrophobic MOFs for biogas upgrading. If we are to focus on the selective capture of just H_2S, we may wish to reconsider some of the assumptions that we have made to target the biogas mixture. We should investigate how would the top candidates change if the gas mixture composition is slightly different to if we have "dry" gas.

The data from the binary GCMC calculations (H_2S/CH_4) on 34 MOF membranes shows adsorption selectivity (*i.e.* ratio of the adsorbate loadings from GCMC simulations at 10 bar in the 50 : 50 mixture) ranging between 26 and 76. These MOFs are very selective to H_2S over CH_4. Although the spread in values may

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† This paper was not presented at the meeting, and the questions were submitted to the authors afterwards.

suggest quite a big difference between the functional features of these MOFs, it is difficult to pinpoint them to a specific type of functional group. One observation is that 4 studied MOFs containing sulfonyl groups ($R–S(=O)_2–R'$) with H_2S/CH_4 adsorption selectivity between 47 and 75. However, we would need to test more structures with sulfonyls groups to be sure of its effectiveness.

If we consider the top 10 based on the values of H_2S/CH_4 adsorption selectivity, they are all relatively different in terms of their chemical composition. However, they do share common geometric properties such as small pore diameters (3.8–6.8 Å), small pore volumes (0.33 to 0.58 g cm^{-3}) and surface areas typically below 1000 m^2 g^{-1}.

Qiaowei Li asked: Are there any common structural features for the top 8 MOFs selected? Do they share similar polar functional groups, or do they have open metal sites?

Elena Besley responded: Table 1 of our paper gives a comprehensive summary of the structural properties of the top 8 MOF membranes. Also Fig. S7† in the updated supporting information now shows the pore structure of the top 8 materials, which appear quite similar in dimensionality. The top membranes are mainly dominated by azole-based heterocycles (5/8). None appear to have open metal sites. Due to limitations of the model to distinguish open metal sites, it is not surprising that we do not observe many in the top candidates. Their separation performance is likely to be underpredicted, and these materials are screened out in early stages.

Conflicts of interest

There are no conflicts to declare.