Supplementary information to
"Modelling the adsorption of short alkanes in protonated chabazite: The impact of dispersion forces and temperature"

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1 Methodology

Different approaches have been proposed to correct DFT calculations for the neglect of dispersion forces. In this work we focus (i) on the semi-empirical PBE-d approach of Grimme[1], (ii) the nonlocal vdW-density-functional of Dion et al.[2], and (iii) the calculation of the dielectric response function in the RPA, combined with the ACFDT for the calculation of the total energy[3, 4].

1.1 Semi-empirical corrections

vdW interactions arise from dynamical dipole-dipole interactions. A spontaneous charge fluctuation in one part of the system induces a dipole at some distant region of space. Such dynamical correlations between electrons are not described in DFT. A semi-empirical correction is provided by adding an energy $E_{\text{disp}}$ described by a sum over pair interactions between atoms located at a distance $R_{ij}$, with a distance-dependence characteristic for dipole-dipole interactions

$$E_{\text{DFT}+d} = E_{\text{DFT}} + E_{\text{disp}}$$

with

$$E_{\text{disp}} = s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_{ij}^6}{R_{ij}^6} \hat{f}_{\text{dmp}}(R_{ij}).$$

The approach was proposed by Grimme and named DFT+d [1]. The $C_{ij}^6$ parameter determines the strength of the pairwise interactions between atoms, it is calculated as the geometrical average

$$C_{ij}^6 = \sqrt{C_i^6 C_j^6}$$

of the $C_6$-factors of atoms $i$ and $j$. The atomic $C_6$ factors can, in principle, be calculated from the polarizabilities of the atoms. In Grimme’s approach the $C_6$ parameters are adjustable parameters fitted to reproduce the results of higher-level quantum-chemical calculations for a large molecular training set. The vdW concept of dispersion forces is properly defined only for the interaction between non-overlapping atomic electron densities. Therefore it is necessary to
use a cut-off function $f_{	ext{drop}}(R_{ij})$ which goes to zero as the atoms start to get too close. For the exact functional form we refer the reader to the original work of Grimme.[1]

The semi-empirical corrections can be applied to DFT calculations with any exchange-correlation functional. The scaling factor $s_{6}$ accounts for the differences in the DFT total energies. In our calculations we used the semi-local gradient-corrected functional of Perdew, Burke, and Ernzerhof (PBE).[5]. For the PBE functional a value of $s_{6} = 0.75$ has been suggested.[1] Because the forces acting on the atoms can easily be calculated, the PBE+d approach allows to optimize the structure of the adsorbate-zeolite complex under the influence of the vdW corrections.

1.2 vdW-DF - A truly nonlocal correlation expression

The vdW-density-functional consists of the semi-local exchange-functional of an appropriately chosen version of the generalized gradient approximation (GGA), the short-range local part of the correlation-functional treated within the local density approximation (LDA), and a long-range nonlocal correlation functional accounting for the vdW effects,

$$E_{xc} = E_{x}^{GGA}[\rho(r), \nabla \rho(r)] + E_{c}^{LDA}[\rho(r)] + E_{c}^{LR}[\rho(r), \rho(r')]$$

(4)

The derivation of the nonlocal part of the correlation functional starts from an approximate form of the coupling-constant integration formula for the total energy and uses a simplified form of the dielectric function in a single-pole approximation. The final form of the functional is

$$E_{c}^{LR} = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' n(r)\Phi(r, r')n(r'),$$

(5)

where the kernel $\Phi(r, r')$ is a function of the electron densities and their gradients at sites $r$ and $r'$ - for all details we refer to Dion et al.[2]. An overview of recent applications of the vdW-DF functional has been presented by Langreth et al.[9].

While both correlation contributions are well defined, the exact functional form of the exchange contribution $E_{x}^{GGA}$ has been the topic of some discussion [6, 7, 8]. In the original paper by Dion et al. it was suggested[2] to use the revised form of the PBE functional (rev-PBE).[10] It was argued that this functional is truly correlation free, and avoids the spurious overbinding characteristic for the LDA and some GGA functionals. We have used this parameterization in our work.

Most applications of the vdW-DF functionals are non-selfconsistent, the approach has been used to determine post-DFT corrections to the total energy at a fixed geometry. For the calculation of the Hellmann-Feynman forces used for a structural optimization of the system, a selfconsistent version of the vdW-DF scheme is required. In a selfconsistent version[11] nonlocality appears also in the exchange-correlation potential in the Kohn-Sham equations

$$V_{c}^{nl}(\mathbf{r}) = \delta E_{c}^{nl}[\rho]/\delta \rho(\mathbf{r}).$$

(6)

The calculation of the Hellmann-Feynman forces with the vdW-density functional has been described by Gulans et al.[6], this method has been used in the present work.
1.3 Random phase approximation

In the random phase approximation (RPA) the exchange-correlation energy is given by

\[ E_{xc} = E_{HF}^{x}([\phi_i]) + E_{RPA}^{c}(\chi^{KS}([\phi_i])) \]  

(7)

where \( E_{HF}^{x} \) denotes the Hartree-Fock exchange energy of the many-electron system with orbitals \([\phi_i]\) and \( E_{RPA}^{c} \) is the RPA correlation contribution which is a functional of the Kohn-Sham response function of the non-interacting electrons \( \chi^{KS}([\phi_i]) \). The correlation energy is calculated from the frequency-dependent dielectric function of the system via a coupling-constant integration. After performing the integration the correlation energy \( E_{RPA}^{c}(\chi^{KS}([\phi_i])) \) is given by

\[ E_{RPA}^{c}(\chi^{KS}([\phi_i])) = -\int_{0}^{\infty} \frac{d\omega}{2\pi} Tr \{ ln[1 - \nu \chi^{KS}(i\omega)] + \nu \chi^{KS}(i\omega) \} . \]  

(8)

In terms of the response-function \( \chi^{KS} \) of the non-interacting system.

In principle the evaluation of the dielectric function requires a summation over all occupied and empty eigenstates. In practical calculations the number of plane waves in the basis set (and with it the number of eigenstates) is finite. To correct for this inaccuracy we use an extrapolation-mechanism that has been well established for the free electron gas (see, e.g., Ref. [3]),

\[ E_{c}(E_{cut}^{\infty}) = E_{c}^{\infty} + \frac{A}{(E_{cut}^{\infty})^{3/2}}. \]  

(9)

In this expression \( E_{cut}^{\infty} \) denotes the energy cut off for the calculations and \( E_{c}^{\infty} \) are the corresponding energies for an infinite energy cut-off. Still a large dependency of total energies on this energy cut-off can be observed, which vanishes when energy differences are considered.[3]

While the self-consistent calculation of RPA energies is in principle possible [12], most often preconverged PBE wave-functions are used in calculations for extended systems. Ren et al.[13] proposed to consider the RPA correlation energies as a correction to self-consistent Hartree-Fock calculations (RPA-HF). Using this approach they were able to minimize errors in calculations.
2 Adsorption geometries of alkanes in protonated chabazite

Table 1: Adsorption geometries for methane, ethane and propane calculated using different levels of theory. This includes the distance (in Å) between the active site and the C atom closest to it (C₁) as well as the distance between the second (C₂) and third (C₃) atom and the closest Si atom. The first line refers to the O(1)-H, the second line to the O(2)-H, the third line to O(3)-H and the fourth line to the O(4)-H adsorption configuration.

|        | PBE | PBE-d | vdW-DF |
|--------|-----|-------|--------|
| Methane|     |       |        |
| C₁-H   | 2.26| 2.16  | 2.46   |
|        | 2.27| 2.12  | 2.69   |
|        | 2.36| 2.23  | 2.62   |
|        | 2.21| 2.14  | 2.44   |
| Ethane |     |       |        |
| C₁-H   | 2.22| 2.14  | 2.40   |
|        | 2.34| 2.36  | 2.62   |
|        | 2.32| 2.23  | 2.50   |
|        | 2.20| 2.13  | 2.34   |
| C₂-Si  | 4.00| 3.79  | 4.05   |
|        | 4.16| 3.86  | 4.34   |
|        | 4.31| 4.08  | 4.26   |
|        | 4.34| 4.06  | 4.39   |
| Propane|     |       |        |
| C₁-H   | 2.33| 2.16  | 2.42   |
|        | 2.38| 2.38  | 2.58   |
|        | 2.28| 2.24  | 2.49   |
|        | 2.31| 2.23  | 2.52   |
| C₂-Si  | 4.48| 3.85  | 4.070  |
|        | 4.39| 3.98  | 4.30   |
|        | 4.23| 4.08  | 4.31   |
|        | 4.63| 4.41  | 4.63   |
| C₃-Si  | 3.88| 4.75  | 4.71   |
|        | 4.06| 3.64  | 3.98   |
|        | 4.69| 4.75  | 4.55   |
|        | 3.93| 3.86  | 3.97   |
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