**Incorporating material flexibility effects into adsorption modeling using non-local Density Functional Theory**

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Among theoretical developments, the molecular density functional theory (DFT) has emerged as one of the most powerful and convenient molecular approach for the description of the thermodynamic properties of inhomogeneous fluids. The development of DFT for classical fluids originates in the late 70’s [1] and its use is nowadays widespread for the description of fluid interfaces or fluids confined in nanopores, the characterization of porous materials [2], etc. The success of DFT approaches is explained by the fact that they preserve detailed information on the microstructure of inhomogeneous fluids but with a much lower computational expense than molecular simulations. Much progress has been made in recent years in the development of both: i) the formulation of more realistic free energy functionals, necessary to account for complex fluids [3], ii) and more efficient numerical algorithms to apply DFT to complex geometries [4]. DFT framework is naturally derived in the Grand Canonical ensemble, which is suitable for fluid adsorption in rigid frameworks while the appropriate thermodynamic ensemble for the treatment of adsorption in flexible porous materials is the osmotic statistical ensemble. Hence, only a very limited number of DFT-based studies addressed the flexibility of the porous network [5,6]. Few years ago, Coudert *et al.* [7] proposed a simplification of the osmotic configurational partition function leading to a tractable formulation of the osmotic potential to study the adsorption in flexible porous materials with molecular simulations. In this work, we use this strategy to address the adsorption of fluids in breathing adsorbents with a NLDFT framework. In particular, the adsorption in a material presenting two distinct shapes (large-pore and narrow-pore) is investigated as a representative example of breathing metal-organic frameworks (such as MIL-53).

**References:**

1. Evans, R. The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform classical fluids, Adv. Phys, 28, (1979) 143–200.

2. Landers, J.; Gor, G. Y.; Neimark, A. V., Density functional theory methods for characterization of porous materials, Colloids Surfaces A Physicochem. Eng. Asp., 437 (2013) 3–32.

3. Miqueu, C. ; Grégoire, D., Estimation of pore pressure and phase transitions of water confined in nanopores with non-local density functional theory, Mol. Phys., 118 (2020) e1742935.

4. Stierle, R. ; Sauer, E.; Eller, J.,; Theiss, M.; Rehner, P.; Ackermann, P.; Gross, J., Guide to efficient solution of PC-SAFT classical Density Functional Theory in various Coordinate Systems using fast Fourier and similar Transforms, Fluid Phase Equilib., 504 (2020) 112306.

5. Ravikovitch, P. I.; Neimark, A. V., Density functional theory model of adsorption deformation, Langmuir, 22(26) (2008), 10864-10868.

6. Evans, J. D.; Krause, S.; Kaskel, S.,; Sweatman, M. B.; Sarkisov, L., Exploring the thermodynamic criteria for responsive adsorption processes, Chemical Science, 10(19) (2019) 5011-5017.

7. Coudert, F. X.; Jeffroy, M.; Fuchs, A. H.; Boutin, A.; Mellot-Draznieks, C., Thermodynamics of guest-induced structural transitions in hybrid organic− inorganic frameworks., Journal of the American Chemical Society, 130(43) (2008) 14294-14302.

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