Modeling breathing of Mil-53: from force fields to thermodynamic insights

Louis Vanduyfhuys, Toon Verstraelen, An Ghysels, Steven Vandenbrande, Ruben Demuynck, Sven Rogge, Rochus Schmid, Guillaume Maurin, Michel Waroquier, Veronique Van Speybroeck

Center for Molecular Modeling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium

Accurate Force Fields for MOFs - QuickFF [1]

AI input

$$\begin{bmatrix} \frac{\partial^2 V}{\partial x_1^2} & \frac{\partial^2 V}{\partial x_1 \partial x_2} & \cdots \\ \frac{\partial^2 V}{\partial x_2 \partial x_1} & \frac{\partial^2 V}{\partial x_2^2} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

- AI geometry in equilibrium
- AI Hessian in equilibrium
- atomic charges (optionally)
- van der Waals parameters (optionally)

QuickFF

$$\min \quad \chi_n^S\left(\vec{R}\right) = \frac{1}{2}\sum_{m\neq n}\left[q_m(\vec{R}) - q_m(\vec{R}_0)\right] \quad \text{with} \quad q_n = \tilde{q}_n$$

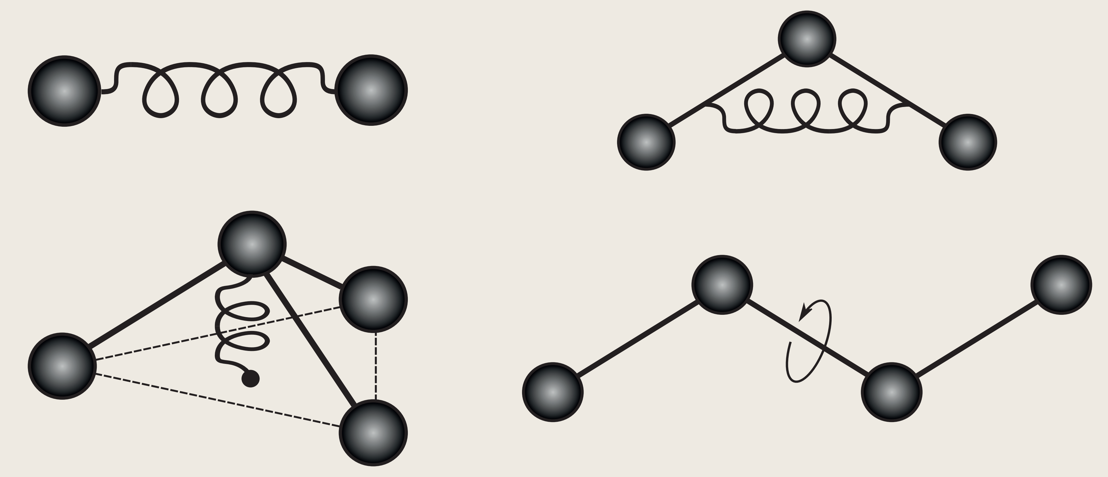
$$V^{\text{ai}}\left(\vec{R}(\tilde{q}_n)\right) = V_{\text{el}}^{\text{ff}}\left(\vec{R}(\tilde{q}_n)\right) + V_{\text{vdW}}^{\text{ff}}\left(\vec{R}(\tilde{q}_n)\right) + \frac{K_n}{2}(\tilde{q}_n - q_{n,0})^2 + c$$

$$\chi^H\left(\vec{K}\right) = \sum_{i\leq j}\left([\boldsymbol{H}^{\text{ai}}]_{ij} - \frac{\partial^2 V_{\text{el}}^{\text{ff}}}{\partial R_i \partial R_j} - \frac{\partial^2 V_{\text{vdW}}^{\text{ff}}}{\partial R_i \partial R_j} - \frac{\partial^2 V_{\text{cov}}^{\text{ff}}}{\partial R_i \partial R_j}(\vec{K})\right)^2$$

Force field parameters estimated in three-step procedure:

1) Estimate dihedral multiplicity and rest value
2) Estimate harmonic parameters from perturbation trajectories
3) Refine force constants by fitting FF Hessian to AI Hessian

FF output

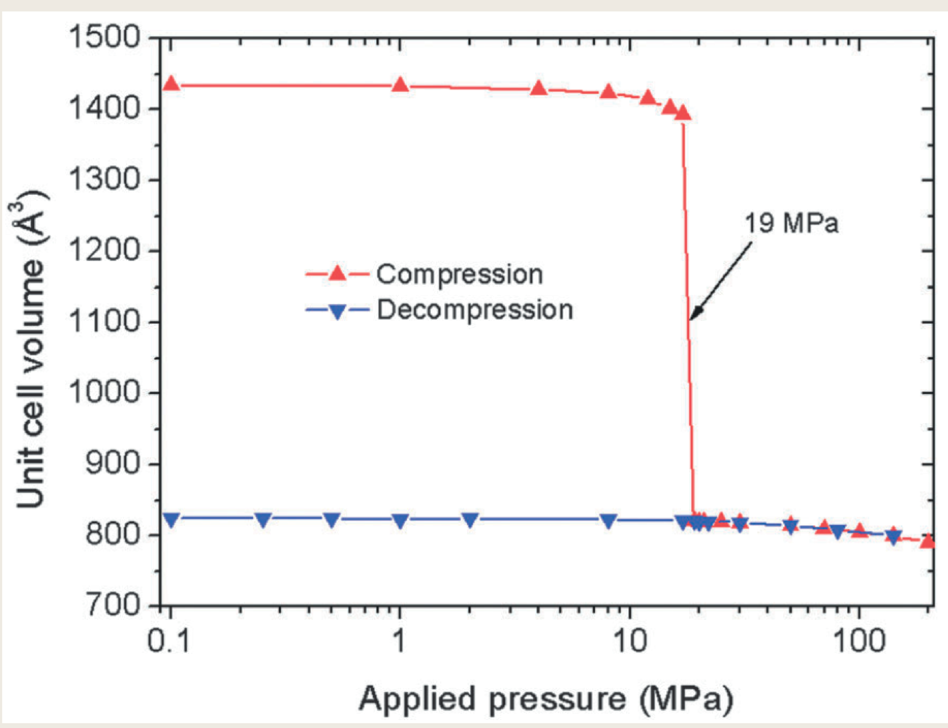


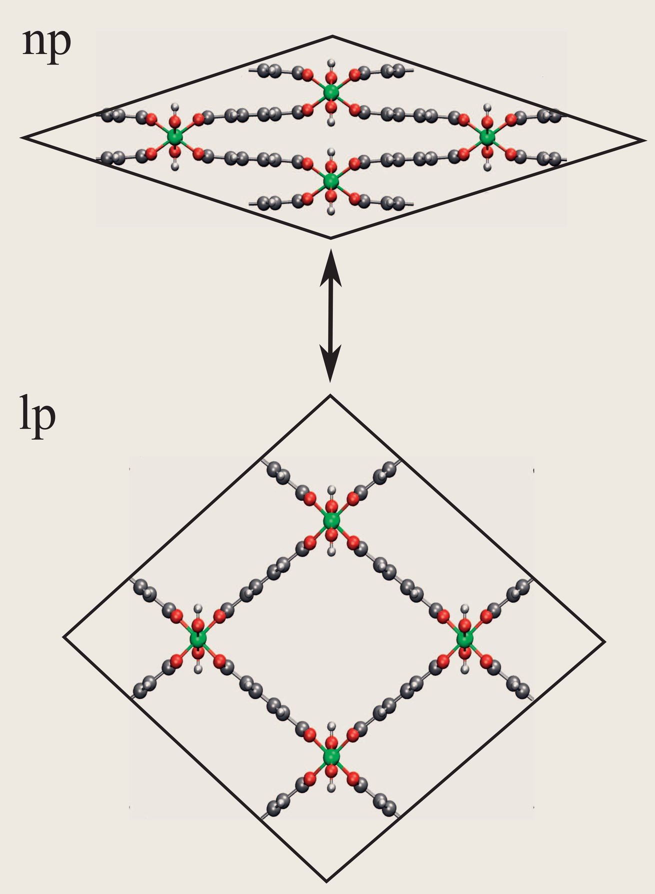
$$V_{\text{cov}}^{\text{ff}} = \sum_{i=1}^{N_r}\frac{K_i^r}{2}(r_i - r_{0,i})^2 + \sum_{j=1}^{N_\theta}\frac{K_j^\theta}{2}(\theta_j - \theta_{0,j})^2 + \sum_{l=1}^{N_d}\frac{K_l^d}{2}(d_l - d_{0,l})^2 + \sum_{k=1}^{N_\phi}\frac{K_k^\phi}{2}[1 - \cos(m_k(\phi_k - \phi_{0,k}))]$$

Flexibility of the empty Mil-53 framework

Volume as function of pressure from NPT simulations with fluctuating unit cell [2].

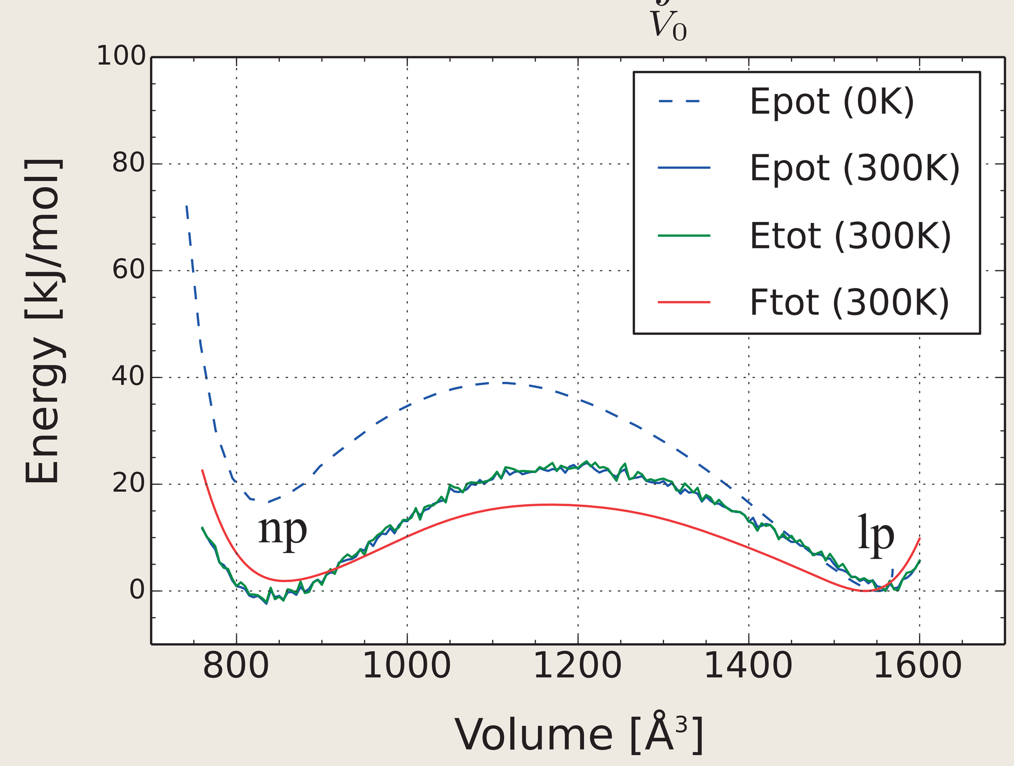
$$V(P) = \left\langle \hat{V} \right\rangle_{NPT}$$





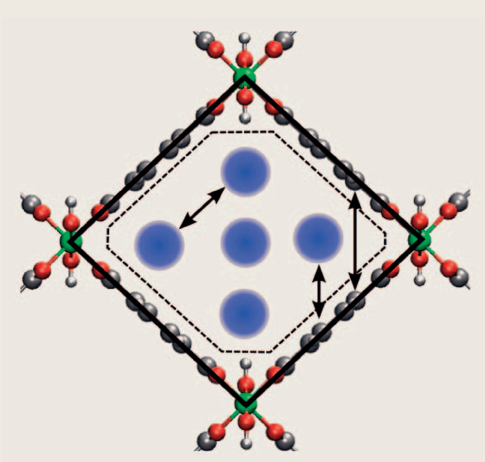
Isotropic pressure as function of unit cell volume from NVT simulations with fluctuating cell shape but fixed volume. [3]

$$F(V,T) = F(V_0,T) - \int_{V_0}^{V} P(V',T)dV'$$



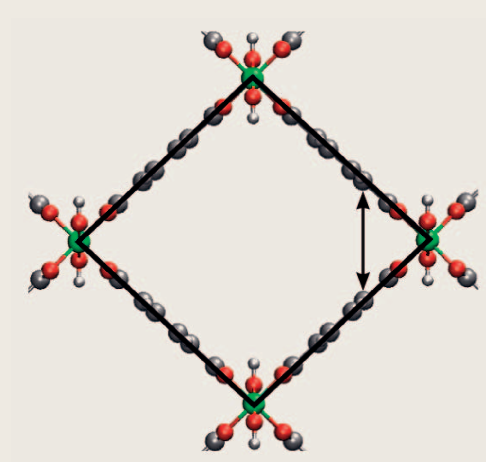
Breathing in Mil-53 under influence of xenon adsorption [4]

Total



=

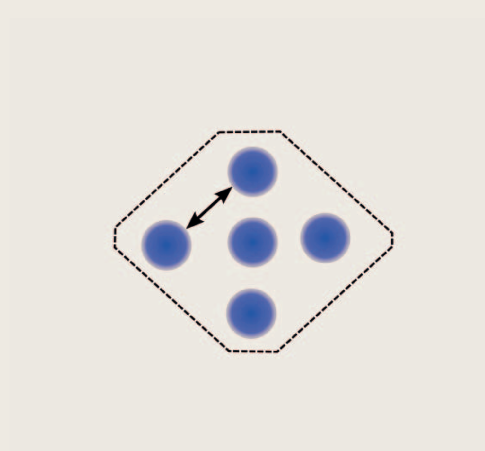
empty host



$$F(V,T) = F(V_0,T) - \int_{V_0}^{V} P(V',T)dV'$$

+

guest molecules

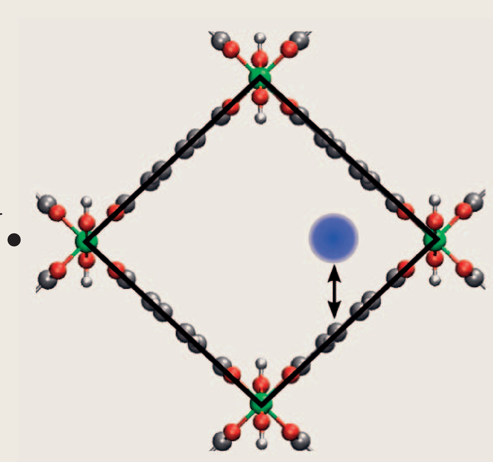


Free energy of van der Waals gas

+

interaction

N·

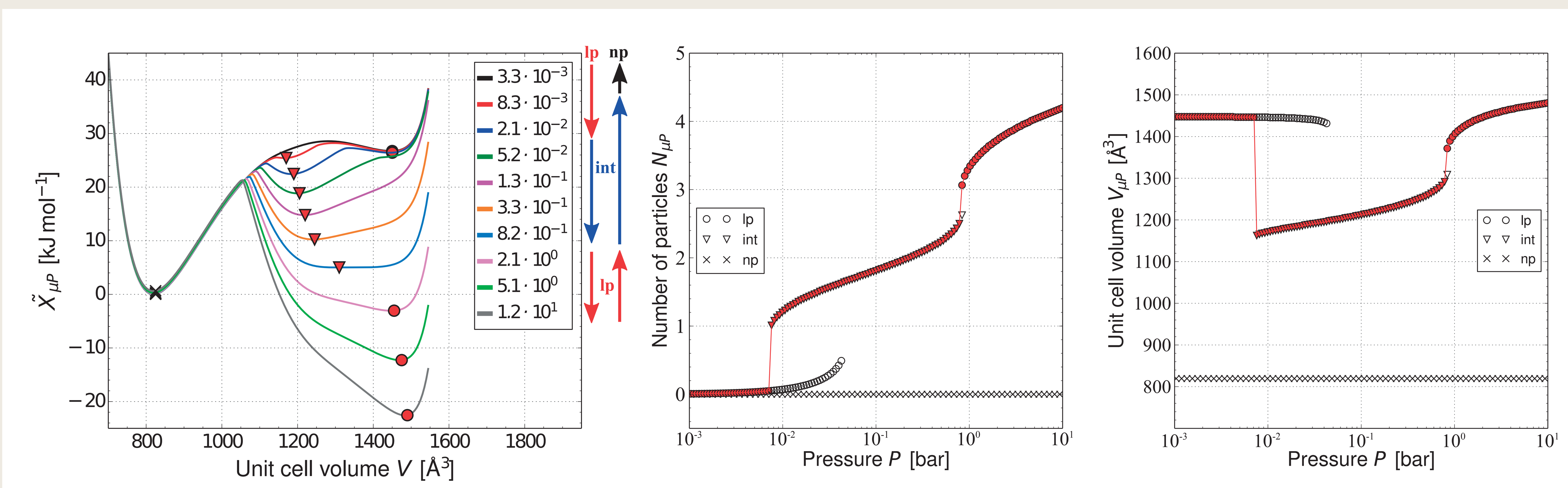


$$F(N,V,T) = N \cdot \frac{\int U_{\text{int}}(R,r)e^{-\beta U_{\text{int}}}dr}{\int e^{-\beta U_{\text{int}}}dr}$$

Transform the canonical ensemble to the osmotic ensemble:

$$\tilde{X}(\mu,P,T;N,V) = F(N,V,T) + PV - \mu N$$

$$\begin{cases} \frac{\partial \tilde{X}}{\partial N} = 0 & \mu = \mu_{\text{guest}}(N,V) + \mu_{\text{int}}(V) \\ \frac{\partial \tilde{X}}{\partial V} = 0 & P = P_{\text{host}}(V) + P_{\text{guest}}(N,V) + P_{\text{int}}(N,V) \end{cases}$$



References

[1] L. Vanduyfhuys, S. Vandenbrande, T. Verstraelen, R. Schmid, M. Waroquier, V. Van Speybroeck, *J. Comp. Chem.*, **2015,** 36, 1015
[2] P.G. Yot, Z. Boudende, J. Marcia, D. Granier, L. Vanduyfhuys, T. Verstraelen, V. Van Speybroeck, T. Devic, C. Serre, G. Ferey, N. Stock, G. Maurin, *Chem. Comm.* , **2014**, 50, 9462
[3] L. Vanduyfhuys et al., **2015**, *in preparation*
[4] L. Vanduyfhuys, A. Ghysels, S.M.J. Rogge, R. Demuynck, V. Van Speybroeck, *Mol. Simulat.*, **2015**, *in press*