

Modelling phase transitions in temperature-responsive flexible metal-organic frameworks: the delicate balance between dispersion and entropy

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The unique combination of metal nodes and organic linkers has endowed some metal-organic frameworks (MOFs) with an unparalleled flexibility. A particularly fascinating example is MIL-53(Al). This so-called breathing framework undergoes a large and abrupt volume change as a function of temperature. However, the underlying physics has thus far remained unclear, prohibiting rational design for sensing and actuator applications.

We show that describing the temperature-dependent phase stability of breathing MOFs requires sophisticated approaches to both dispersion interactions and entropic effects. Standard dispersion-corrected density-functional methods do not describe the low-temperature stability of the small-volume phase of MIL-53(Al) correctly. We have applied the random-phase approximation to the correlation energy, including single-excitation corrections, and were able to show that many-body dispersion effects are crucial to get the relative phase stability at 0 K right. On the other hand, higher temperatures increase the role of entropy, which promotes the stability of a large-volume structure. We compared different advanced thermodynamic sampling schemes to reconstruct the free energy landscape as a function of temperature. We find that for MIL-53(Al), umbrella sampling with the weighted histogram analysis method provides the best tradeoff between speed and precision.

[1] J. Wieme, K. Lejaeghere, G. Kresse, V. Van Speybroeck, “Tuning the balance between dispersion and entropy to design temperature-responsive flexible metal-organic frameworks”, submitted.

[2] R. Demuynck, S.M.J. Rogge, L. Vanduyfhuys, J. Wieme, M. Waroquier, V. Van Speybroeck, “Efficient Construction of Free Energy Profiles of Breathing Metal-Organic Frameworks Using Advanced Molecular Dynamics Simulations”, *JCTC* 13, 5861-5873 (2017).