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Origins of Negative Gas Adsorption

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SUMMARY

Negative gas adsorption by a porous crystalline solid, DUT-49, observed by spontaneous desorption of gas during a pressure increase, raises fundamental questions on the physical origin of this puzzling behavior. Importantly, a framework able to transform a large amount of strain into pressure has many possible technological applications. To address this question, we have performed a combined study of the mechanics and thermodynamics of DUT-49 at both the molecular unit and framework scales, employing quantum density functional theory and extensive classic molecular dynamics simulations. We demonstrate that negative gas adsorption takes its origin from a molecular buckling of the organic structural unit, allowing a colossal framework transformation. Methane adsorption is subsequently shown to activate this transition, in full agreement with experimental observations. The molecular insight, presented here, has unveiled the mechanics and thermodynamics responsible for negative gas adsorption and provides unparalleled understanding to aid the discovery of new examples of similarly responsive porous metamaterials.

Keywords: nanoporous materials, thermodynamics, mechanics, gas adsorption, methane, stimuli-responsive

The Bigger Picture

Conventional nanoporous materials have a wide range of technological applications as desiccants, ion exchangers and catalysts. However, it is increasingly evident that emerging flexible metal-organic framework materials are particularly advantageous in separation processes and responsive applications. In particular, the flexible material DUT-49 shows an unexpected

phenomenon where, as the material fills with gas, it contracts suddenly and releases a significant portion of methane. This negative gas adsorption process is extremely rare and has not been observed in porous materials previously. Here, we demonstrate the mechanics and thermodynamics responsible for this non-conventional behavior using multi-scale computer simulations. This fundamental understanding is crucial for the application of negative gas adsorption materials, such as advanced micro-pneumatic components and stimuli-responsive separation processes.

1 Introduction

2 Metal-organic frameworks (MOFs) differ from conventional inorganic porous
3 materials in that many demonstrate large-scale flexibility of their structure,
4 which results in appealing physical and chemical properties.[1] Notably, there
5 are increasing reports of these soft porous crystals[2] whose flexibility man-
6 ifests by large-scale transformations induced by modest physico-chemical
7 stimulation, such as changes in temperature, mechanical constraints, and
8 guest adsorption.[3] Among the large variety of behavior exhibited by stimuli-
9 responsive materials, we can cite the widely studied phenomena of gated
10 adsorption and breathing,[4] which have applications in gas separations,[5]
11 storage[6] and sensing.[7]

12 A particularly intriguing phenomenon resulting from this soft nature
13 of metal-organic frameworks (MOFs) is that of negative gas adsorption
14 (NGA) in DUT-49, which was recently reported by Kaskel and coworkers.[8]
15 DUT-49 is a MOF constructed from dinuclear paddlewheel copper(II) metal
16 centers and 9,9'-([1,1'-biphenyl]-4,4'-diyl)bis(9H-carbazole-3,6-dicarboxylate
17 (BBCDC) linkers, forming a cubic mesoporous framework displayed in Fig-
18 ure 1a.[9] Laws of thermodynamics mandate that, at equilibrium and at
19 constant temperature, the absolute amount of substance in the adsorbed
20 phase increases with increasing pressure of the adsorbate, which results in
21 the positive slopes observed for single-component adsorption isotherms.[10]
22 However, upon adsorption of gases such as methane or *n*-butane, DUT-49
23 displays a NGA step depicted in Figure 1b, causing an unexpected pressure
24 amplification triggered by a sudden structural transition of the nanoporous
25 framework. It is the first material known to exhibit this property, which was
26 attributed to the filling of the micropores by guests and the occurrence of a
27 metastable state of the loaded framework. However, there has been so far

28 no direct account of the microscopic nature of the transition itself, and the
29 detailed balance of thermodynamic driving forces is unknown.

30 *In situ* X-ray diffraction was used to elucidate the open pore (*op*) and
31 contracted pore (*cp*) structures of DUT-49 as depicted in Figure 1a. The
32 structural transformation observed in this material — linked to the NGA
33 — is localized to a deformation of the BBCDC ligand, Figure 1c. This is in
34 stark contrast with previously known examples of large structural transitions
35 in MOFs, where organic linkers are seen as rigid struts. Commonly, flexible
36 MOFs rely upon either a hinging mechanism, where the deformation occurs in
37 the coordination of the metal node,[11, 12, 13] or sub-lattice displacement[14]
38 as stylistically illustrated in Figure 1d. Moreover the periodic array of ge-
39 ometrically and elastically coupled buckling units in DUT-49 is analogous
40 to the folding and unfolding of maps, wings, petals and the artificially con-
41 structed Miura-ori pattern.[15, 16] We thus hypothesize the deformation ob-
42 served for the ligand, and the collective behavior coupling these deformations
43 throughout the crystal, is crucial to the NGA phenomenon allowing for an
44 accessible, rapid, and large structural transformation.

45 Herein, we detail multiscale molecular simulations of DUT-49 to provide
46 insight into the mechanics and thermodynamics of the NGA transition, link-
47 ing this astonishing macroscopic behavior to a mechanism at the atomistic
48 scale. We combine quantum chemistry calculations at the density functional
49 theory (DFT) level with classical molecular dynamics simulations to provide
50 a complete picture of this phenomenon.

51 **Results and Discussion**

52 To provide understanding at the microscopic level of the negative gas
53 adsorption transition, we combined a variety of methods including DFT cal-
54 culations of the vital components of the DUT-49 framework and classical
55 simulation of the crystal and adsorbates.

56 *Ligand mechanics*

57 Initial investigation of the experimental crystal structures of DUT-49,
58 *op* and *cp*, shows that the copper paddlewheel environment is almost un-
59 deformed in the *cp* structure, while the BBCDC ligand is significantly bent
60 — with the deformation localized on the biphenyl unit. This behavior of
61 the ligand is akin, in the world of macroscopic mechanics, to the buckling
62 of a column upon the application of a critical load.[17] The phenomena of

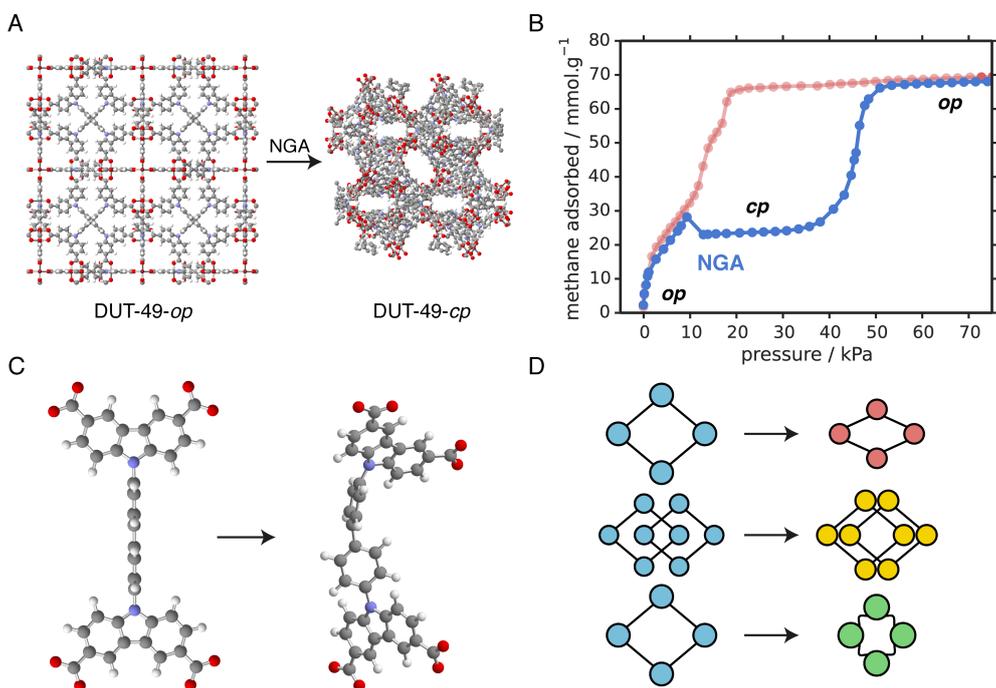


Figure 1: A summary of the crystal structure of DUT-49-*op* (open pore) and DUT-49-*cp* (contracted pore) including the transitions present during negative gas adsorption (NGA) and subsequent pore saturation (A). An example of the experimental isotherm observed for DUT-49 during methane adsorption at 111 K (B, blue) and the type 1 isotherm, calculated by simulation, for the static DUT-49-*op* structure (B, red).[8] Buckling-like deformation of the BBCDC ligand demonstrated during the NGA process (C). Stylistic representation of structural transformations in MOFs: hinging mechanism (red), sub-lattice displacement (yellow) and the mechanism observed in DUT-49 (green).

63 buckling is characterized by a sudden sideways failure of a structure sub-
 64 jected to significant axial compressive stress, where the compressive stress
 65 at the point of failure is less than the ultimate compressive stress that the
 66 material is capable of withstanding. To test the relevance of this analogy,
 67 we performed DFT optimizations of a single isolated ligand with a series of
 68 fixed decreasing N atom to N atom distance. All other internal coordinates
 69 were freely optimized. By derivating the energy–strain curve, we obtain a
 70 stress–strain profile depicted in Figure 2. Moreover, the constrained struc-
 71 tures clearly reflect the dihedral like rotation of carbazole moieties when the
 72 linker is compressed and bends, as observed in the experimental contracted

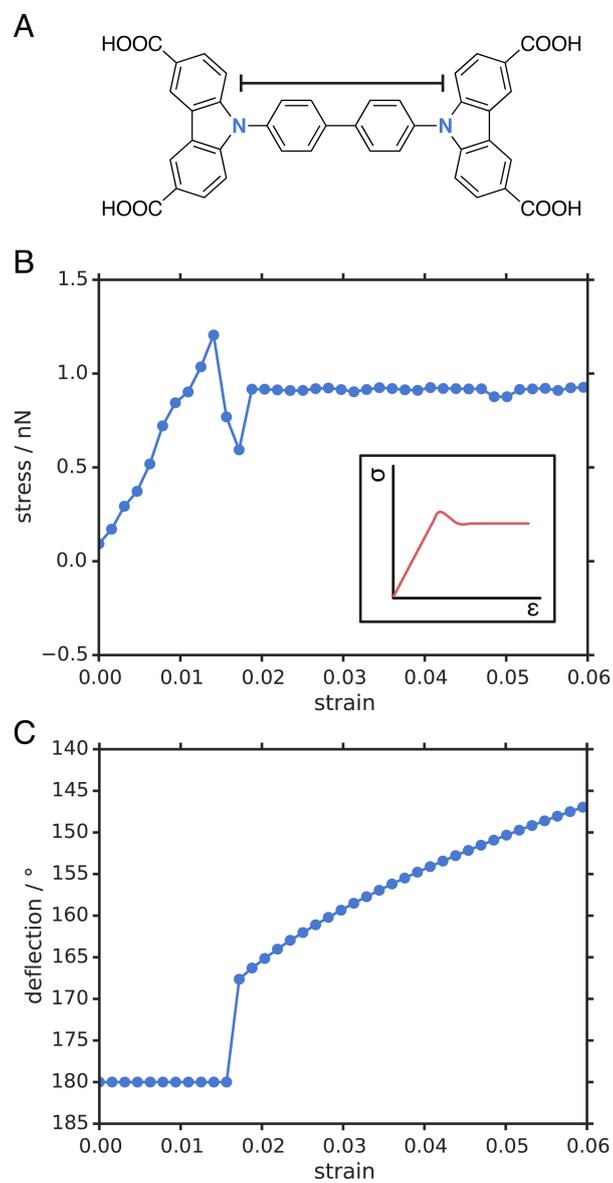


Figure 2: (A) BBCDC ligand with the N atom to N atom distance highlighted. (B) Stress-strain curve of the BBCDC ligand relative to axial compression; in inset, a typical stress-strain curves found for macroscopic materials with buckling.[17] (C) Deflection angle of the ligand, measured as N-centroid-N angle.

73 pore structure. We quantify the bending of the linker by a “deflection” pa-
74 rameter, which we take as the N–centroid–N angle.

75 Figure 2 reveals two distinct regimes upon the application of strain to the
76 ligand. Firstly, small deformations result in no deflection as the ligand retains
77 a linear structure. This elastic regime merely corresponds to the compression
78 of interatomic bonds with, as expected, a linear response to deformation. For
79 deformations greater than 3 Å a buckling transition occurs, with a sudden
80 large deflection of the ligand and a non-linear mechanical response. Initially,
81 by only considering the static structures of DUT-49-*op* and DUT-49-*cp* the
82 energy cost of 91 kJ.mol⁻¹ per ligand appears to be a significant penalty to
83 the transformation. However, the analysis provided here shows the critical
84 event requires significantly less energy at 10 kJ.mol⁻¹. Subsequently, upon
85 the onset of buckling the ligand continues to collapse at constant stress.

86 The buckling of the ligand is in all features similar to that observed for
87 macroscopic materials (represented as inset of Figure 2b). This elastic re-
88 sponse of the ligand, which has not been previously observed in MOFs, pro-
89 duces a bending-dominated framework which is observed commonly with
90 foam lattice-structured materials.[18] A consequence of the buckling feature
91 in these materials is their stiffnesses are significantly reduced to that expected
92 of stretch-dominated structures. For example, a typical foam with buckling
93 behavior is less stiff by a factor of 10 than a stretch-dominated framework
94 of the same density.[18] This mechanical perspective demonstrates how with
95 modest stress the BBCDC ligand buckles thus producing an accessible path-
96 way to a colossal change in volume of the DUT-49 structure.

97 *Structural description and energetics*

98 While DFT calculations show how the mechanical behavior of the organic
99 ligand allow for the structural transition to take place, simulations are re-
100 quired at a larger scale to unveil the precise thermodynamics of NGA. Owing
101 the large size of the DUT-49 unit cell, with 1 836 atoms, simulations at the
102 DFT level have proved computationally prohibitive. We have thus used clas-
103 sical molecular dynamics simulation to capture the structure, energetics, and
104 dynamics of the transition. The force field was based on the high-accuracy
105 MOF-FF force field, which is known perform extremely well for MOFs and
106 frameworks based on copper paddlewheels in particular. This was extended
107 using MM3 for the organic parts (such as biphenyl unit) not available in
108 MOF-FF.[19, 20]

109 To ensure the accuracy of the classical simulation methodology used here,
110 we first generated trajectories of DUT-49-*op* and DUT-49-*cp* using initial
111 configurations from DFT optimized structures. The 5 ns (N, P, T) simula-
112 tions at 300 K and 1 atm demonstrate that the chosen potential parameters
113 accurately describe the geometry and framework characteristics of both the
114 open and contracted pore forms of the structure. We find that MOF-FF
115 reproduces the unit cell parameters within $\approx 3\%$ of the experimental values
116 for both the open and contracted pore structures. Additional details can be
117 found in the Supporting Information. Notably, these differences are quite
118 small considering that the force field was not adjusted on experimental data
119 for DUT-49, and illustrates that the force field is applicable to both the open
120 and contracted pore forms without scaling or further adjustment.

121 Furthermore, we computed a breakdown of the energy balance between
122 the *op* and *cp* phases of DUT-49 in terms of various contributions to the
123 average total energy, plotted in Figure 3: van der Waals (dispersion and
124 repulsion) interactions, bond stretching, bending, torsion, and out-of-plane
125 energies. This analysis, which can be performed due to the analytical nature
126 of the interactions described by the force field, clearly illustrates the balance
127 of intramolecular strain (dominated by torsion energy and favoring the *op*
128 structure) and intermolecular dispersive interactions (favoring the *cp* struc-
129 ture) which results in a significantly smaller energy penalty to the distorted
130 DUT-49-*cp* structure. Overall, we find that the *op* phase is energetically
131 more stable than the *cp* phase (by 270 kJ.mol⁻¹ per unit cell) in the absence
132 of adsorbate, which is in line with experimental data.

133 *Transition dynamics*

134 We next turn to the description by molecular simulations of the actual
135 transition between the two metastable structures *op* and *cp* of DUT-49. Ex-
136 perimentally, Kaskel and coworkers have shown that these structural tran-
137 sitions can be caused by adsorption and desorption of guest molecules.[8]
138 Because the stable form of the evacuated material at ambient conditions
139 is that with largest volume (*op*), it is expected from thermodynamics that
140 the *op*→*cp* transition can also be triggered by application of external pres-
141 sure — as is the case for the “breathing” transition in MIL-53 and MIL-47
142 materials.[12, 21]

143 In order to check this hypothesis and observe the transition dynamics
144 in the simplest possible case, without adsorbate, we performed constant-
145 pressure simulations where the pressure applied was varied over time. The

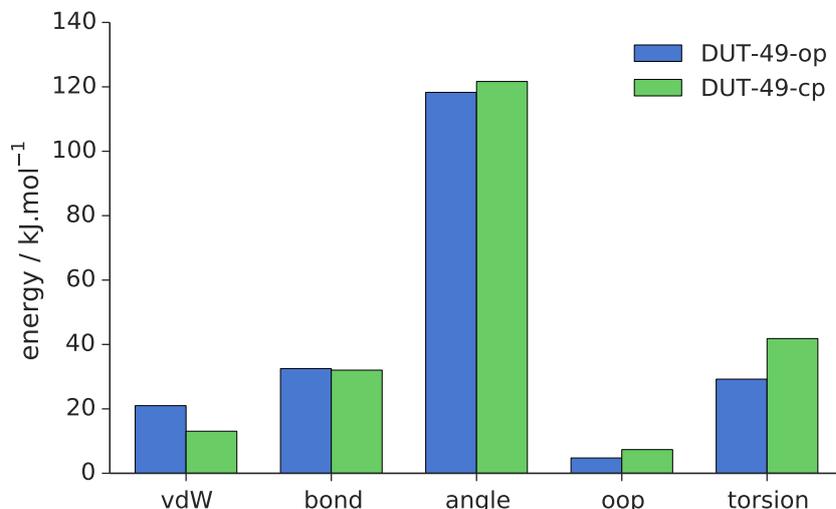


Figure 3: Average energy contributions, per ligand, for van der Waals (vdW), bond stretching, angle bending, out of plane (oop) and torsion terms during (N, P, T) simulations of guest-free DUT-49-*op* and DUT-49-*cp* at ambient conditions.

146 simulation trajectories, all conducted at 300 K, start from the *op* phase. They
 147 consist of 0.5 ns of initial equilibration at atmospheric pressure, a compression
 148 period with constant isotropic pressure $+P$ for 0.5 ns, additional equilibration
 149 at atmospheric pressure for 1 ns, a decompression (or tension) period with
 150 negative pressure $-P$ for 0.5 ns and a final equilibration at atmospheric
 151 pressure for 1 ns.

152 At modest pressure we only test the elastic behavior of the *op* structure
 153 upon compression and tension, with small variations in unit cell volume as
 154 can be seen on Figure 4a for $P = 50$ MPa (light blue curve). However,
 155 with pressure increments equal to or larger than $P = 60$ MPa, we see that
 156 the NGA transition is observed. The *op* \rightarrow *cp* transition is observed upon
 157 compression the compression stage, confirming the possibility to trigger the
 158 NGA transition with a mechanical constraint. Upon release of the pressure,
 159 we find that the *cp* structure is retained, confirming its metastability in
 160 line with experimental findings. And finally, upon the application of equal
 161 opposite stress (negative pressure) the DUT-49-*op* structure is recovered.

162 To confirm the transformation is the result of the buckling of the BBCDC
 163 ligand, as described previously, the evolution of critical bond parameters were
 164 charted, displayed in the Supporting Information. We observe no significant

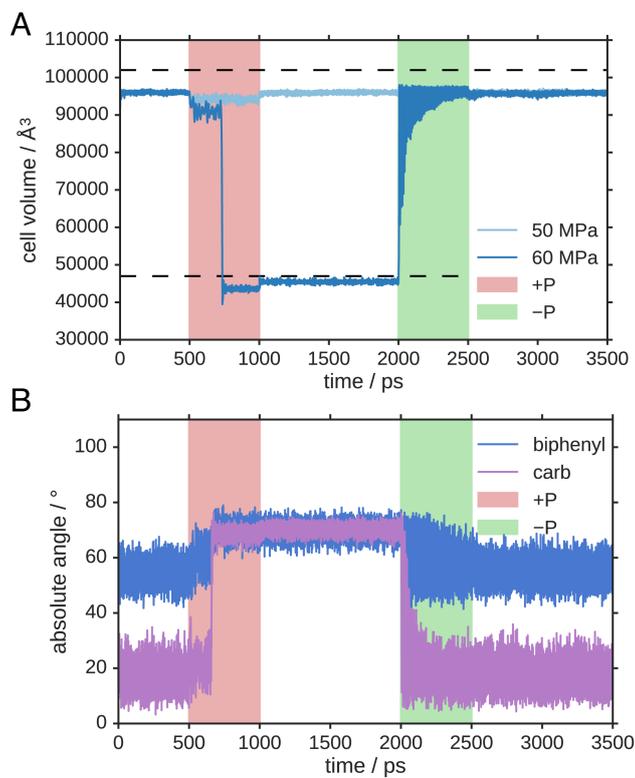


Figure 4: (A) Evolution of the unit cell volume during (N, P, T) simulations of DUT-49, with durations of applied pressure for a pressures of ± 50 and ± 60 MPa (see text for details). The volumes of op and cp phases at ambient conditions are indicated by dotted lines. (B) Averaged absolute dihedral angles of the biphenyl and carbazole (carb) moieties of the BBCDC ligand during these simulations.

165 changes in mean or standard deviation in bond lengths of Cu–Cu, Cu–O
 166 and C–N. However, we find significant and abrupt changes in N–N distances,
 167 biphenyl dihedrals and carbazole dihedrals during the trajectory, which are
 168 depicted in Figure 4b. These structural features are caused by buckling of
 169 the ligand, with the other features remaining invariable. Additionally, as
 170 found for the initial ambient condition simulations, the accounting of energy
 171 contributions during the trajectory explicitly illustrates the balance of energy
 172 between unfavorable torsional strain and favorable dispersion interactions.

174 For solids with multiple phases and structural transitions, the analysis of
 175 their free energy as a function of volume, $F(V)$, yields crucial insight into
 176 the relative stability and metastability of the respective phases. This was,
 177 for example, recently applied to the case of adsorption in the “breathing”
 178 MOF MIL-53(Al).[22] In practice, the $F(V)$ curve can be calculated by ther-
 179 modynamic integration of the internal pressure of the system as a function
 180 of volume. Several constant-volume (N, V, T) MD simulations are performed
 181 to obtain the internal pressure at each point, $P_i(V)$, in the range of volumes
 182 studied. Thus the free energy profile is derived as:

$$F(V) - F(V_{\text{ref}}) = - \int_{V_{\text{ref}}}^V \langle P_i(V') \rangle dV' \quad (1)$$

183 where we chose as reference volume V_{ref} the open pore structure. The re-
 184 sulting profiles of internal pressure and free energy landscapes are plotted
 185 on Figure 5. In addition, the internal energy U was also calculated at each
 186 point.

187 The pressure profile of DUT-49 (Figure 5a) reveals the stable and metastable
 188 structures found at a given external pressure. Crystal structures of the two
 189 distinct phases of DUT-49 were measured at atmospheric pressure and ac-
 190 cording to the profile, three structures correspond to this pressure: the open
 191 pore form, the contracted pore form, and a transition state situated between
 192 these. However, the positive derivative ($\frac{\partial P}{\partial V}$) observed at the transition state
 193 makes it mechanically unstable. Further analysis of this pressure landscape
 194 also predicts how the DUT-49 structure evolves when decreasing or increas-
 195 ing the external pressure as, at mechanical equilibrium, the internal pressure
 196 is equivalent to the external pressure. For pressures above ≈ 60 MPa, we find
 197 only one stable state exists where the system remains the contracted pore
 198 state. Contrastingly, DUT-49 exists as the large pore structure for pressures
 199 below ≈ -60 MPa. In between, the two phases are metastable, in line with
 200 both experimental data and the results of direct molecular dynamics under
 201 pressure.

202 Notably, the pressure required to achieve buckling (≈ 60 MPa) is in
 203 the range of adsorption-induced stresses, exerted by adsorbed fluids on the
 204 solid.[23] Thus it is unsurprising that the transition $op \rightarrow cp$ is observed dur-
 205 ing gas adsorption experiments.

206 The free energy profile generated for DUT-49 (Fig. 5b) shows two distinct
 207 minima corresponding to the contracted and open pore structures. Addition-
 208 ally, there exists a energetic barrier of $\Delta F^\ddagger = 130 \text{ kJ.mol}^{-1}$ to the contracted
 209 to open pore transition which prohibits the contracted structure from spon-
 210 taneously opening to the large pore structure without external stimuli. This
 211 mirrors experimental observations in which stress by gas adsorption at sat-
 212 uration is required to regenerate the open pore structure.[8] A free energy
 213 difference between the two phases of $\Delta F = 1\ 010 \text{ kJ.mol}^{-1}$ is predicted (per
 214 unit cell). The magnitude of this difference is in good agreement to the
 215 $2\ 184 \text{ kJ.mol}^{-1}$ energy difference reported previously using DFT methods,
 216 despite the two totally different approaches and level of theory.

217 Finally, the entropy of the DUT-49 structural transition can be estab-
 218 lished by comparing the free energy and internal energy profiles obtained from
 219 the classical molecular simulation, demonstrated in Figure 5b, as $F = U -$
 220 TS . Remarkably, we find that the role of entropy is small in the transition,
 221 which is mainly driven by energetic contributions. The entropy difference be-
 222 tween the *op* and *cp* phases is calculated to be $\Delta S = 0.0433 \text{ kJ.mol}^{-1}.\text{K}^{-1}$,
 223 and entropy plays a larger role in the free energy barrier to the transition
 224 ($\Delta S^\ddagger = 0.184 \text{ kJ.mol}^{-1}.\text{K}^{-1}$). This is in stark contrast with the structural
 225 transitions previously observed in “breathing” MOFs, where the flexibility
 226 is based on a hinging mechanism and deformation of coordination at the
 227 metal center. In those materials, which have been extensively studied from
 228 the thermodynamic point of view, the transition is known to be linked to a
 229 balance between energetic and entropic criteria.[24, 25] Thus, one outcome
 230 is that temperature has little effect on the relative energies of the phases of
 231 DUT-49, and the transition cannot be triggered by changes in temperature,
 232 unlike in MIL-53 materials.

233 *Transition upon gas adsorption*

234 After demonstrating that the structural transition in DUT-49 can be trig-
 235 gered by mechanical pressure in a guest-free framework, and given insight into
 236 its thermodynamics, we now turn to understanding the thermodynamics of
 237 adsorption for the novel phenomenon of negative gas adsorption. By combin-
 238 ing free energy simulations, as described previously, with increasing amount
 239 of methane present in the simulation cell we are able to chart the stability
 240 of the two phases at various points over the entire isotherm. (N, V, T) sim-
 241 ulations were this time performed at 120 K, comparable to the conditions
 242 observed for NGA, with methane loadings of 200, 400, 600, 800 and 1000

243 molecules per unit cell. Subsequently, these simulations result in valuable
 244 thermodynamic information, including variation of the free energy profiles
 245 as illustrated in Figure 6.

Table 1: Differences in total energy (U, kJ.mol⁻¹), free energy (F, kJ.mol⁻¹) and entropy (S, kJ.K⁻¹mol⁻¹) for the transition DUT-49-*op*→DUT-49-*cp*, calculated from *NVT* simulations at 120 K with increasing amount of methane molecules (molecules per unit cell).

CH ₄ adsorbed	ΔU	ΔF	ΔS
0	1 020	1 010	0.0833
200	68.6	234	-1.38
400	-979	-57.1	-7.68
600	-155	1 380	-12.8
800	2 390	8 360	-49.8
1 000	17 100	26 000	-74.2

246 Upon methane adsorption, DUT-49 begins in the *op* phase as this cor-
 247 responds to most energetically favorable phase. However, as the methane
 248 loading increases up to 400 molecules per unit cell (20.2 mmol.g⁻¹), the
 249 *cp* phase is stabilized and becomes the most thermodynamically favorable
 250 phase. This is due to the host-guest interactions being more favorable in
 251 the contracted structure, due to smaller wall-wall distances, and the low
 252 entropic cost corresponding to this loading of methane (Table 1). Despite
 253 this shift in global minima there remains a significant barrier, of the order of
 254 300 kJ.mol⁻¹, associated with the *op*→*cp* transition. Upon further methane
 255 adsorption to 600 molecules per unit cell (30.4 mmol.g⁻¹) the barrier to tran-
 256 sition decreases to \approx 180 kJ.mol⁻¹ allowing the structure to explore higher
 257 density phases. Importantly, we find the free energy landscape for this load-
 258 ing does not include a minima at the *cp* phase as there is significant entropic
 259 expense to condensing the quantity of methane in a low capacity pore struc-
 260 ture. We thus conclude that by undergoing NGA, releasing methane from
 261 the structure, the structure can transform from a metastable state, at 600
 262 molecules per unit cell to a stable *cp* phase, at 400 molecules per unit cell.

263 Finally, as the amount of methane increases to saturation the low ca-
 264 pacity *cp* state is unfavorable due to guest-guest and guest-wall short-range
 265 repulsion; the stable structure at these loadings is then the highly porous *op*
 266 phase, accounting for the “reopening” *cp*→*op* transition. This thermody-
 267 namic analysis, presented here, allows us to provide a precise understanding
 268 of the structural transformations during gas adsorption. In addition, we

269 demonstrate an interplay between the driving forces of the framework and
270 the adsorption process, which gives rise to NGA.

271 **Conclusion**

272 We have used a multiscale computational approach to shed light into the
273 energetics, dynamics and thermodynamics of the negative gas adsorption
274 phenomenon in highly flexible MOF DUT-49. By using DFT simulations we
275 find that the complex yet compliant structure of the DUT-49 ligand allows for
276 its buckling upon modest stress. The elastic coupling of these buckling units
277 allows for the large-scale structural transformation of the entire framework,
278 which is thus significantly softer than would be expected for rigid building
279 units. This microscopic mechanism for flexibility is entirely new and presents
280 a great contrast with previously known flexible MOFs, which relied either on
281 sub-lattice displacement or hinging around metal nodes — with rigid linkers.

282 Furthermore, we have investigated the NGA transition using molecular
283 dynamics simulations. We demonstrated that NGA requires a bistable porous
284 material where the empty open pore (*op*) phase is thermodynamically more
285 stable, but the contracted pore (*cp*) phase is metastable at ambient condi-
286 tions. In addition to this generic criteria, which many “breathing” MOFs
287 may exhibit, negative gas adsorption, requires the relative stability of *cp* and
288 *op* phases to change with gas adsorption. Specifically, we expect the de-
289 creased transition barrier, observed for DUT-49 at 600 molecules per cell of
290 methane, accompanying the absence of a minima at the *cp* volume to be a
291 crucial feature of this process. We also showed that the structural transition
292 in DUT-49 can be triggered by purely mechanical constraints, in the absence
293 of guest molecules.

294 The insight provided by this investigation has elucidated the mechanics
295 and thermodynamics that govern the phenomenon of negative gas adsorption,
296 and will undoubtedly aid in the discovery of other systems with this desirable
297 property.

298 **Simulation Methods**

299 The behavior and mechanical properties of the BBCDC ligand were in-
300 vestigated, for the corresponding acid, using DFT optimizations employed
301 by the CRYSTAL14 software[26] with localized TZVP basis sets[27] and the

302 hybrid exchange–correlation functional PBE0.[28] Long-range dispersion cor-
303 rections were included by using the Grimme “D2” approach.[29] The ligand
304 structure was strained by decreasing the N atom to N atom length from the
305 local minima at 9.827 Å to 9.227 Å, in 40 steps. At each step the structures
306 were optimized with the N atom to N atom length held fixed. Consequently,
307 a stress-strain curve relative to this axial deformation of the ligand was gener-
308 ated, where stress is defined by the gradient of energy and strain the relative
309 decrease in N atom to N atom length.

310 Initial periodic structures of DUT-49-*op* and DUT-49-*cp*, which corre-
311 spond respectively to the open pore (*op*) and contracted pore (*cp*) structures,
312 were obtained from DFT optimized models reported by Krause *et al.*[8] Clas-
313 sical simulations used the MOF-FF forcefield to describe the unsaturated Cu
314 paddlewheels present in the structure.[30] Parameters missing from MOF-
315 FF, for the description of the ligand and methane, were taken from the MM3
316 forcefield for organic molecules, which is itself the basis of MOF-FF.[19, 20]
317 Importantly, we have treated the dihedral parameters of the ligand as to
318 allow unrestricted rotation of the phenyl groups that make up the biphenyl
319 section. Classical molecular dynamics simulations were undertaken using the
320 `pydlpoly` software by Schmidt and coworkers,[31] a Python-wrapped version
321 of `DL_POLY Classic`. [32] To first ensure the accuracy of the force field and
322 potential parameters chosen, (N, P, T) simulations were completed for DUT-
323 49-*op* and DUT-49-*cp*. We then studied the NGA transition by perform-
324 ing series of (N, V, T) simulations at varying guest loading N and volume
325 V . Constant-volume simulations were used to compute the average internal
326 pressure for a given volume, with an initial 100 ps for equilibration and the
327 final 500 ps sampled to obtain a converged value of internal pressure.¹ From
328 a series of constant-volume simulations we could thus integrate the internal
329 pressure to find free energy profiles as a function of volume.[22] This was
330 repeated with the addition of increasing number of methane molecules to the
331 simulation cell, which were grown in during initial equilibration. All classical
332 molecular dynamics simulations used a time step of 1 fs and employed the
333 Nosé-Hoover thermostat and barostat,[33, 34] for the (N, P, T) simulations,
334 with a thermostat relaxation time of 1 ps and barostat relaxation time of

¹We note previous work on the mechanical characterization of MIL-47(Al), the ($N, V, \sigma_a = 0, T$) ensemble was used which allows for the cell shape to change during the simulation.[22] However, as this transition does not involve a change in cell shape (cubic to cubic transition) the use of (N, V, T) simulation is appropriate.

335 2 ps.

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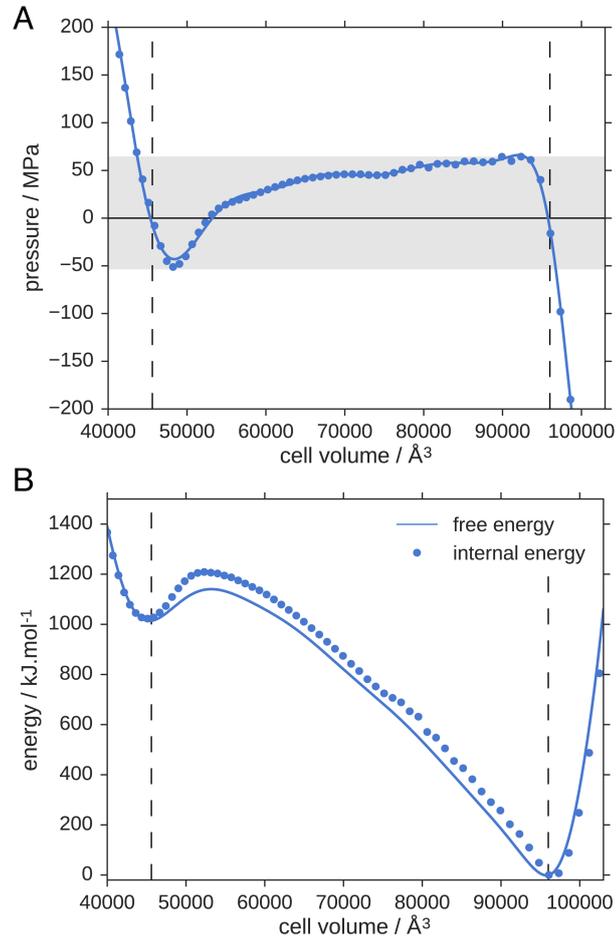


Figure 5: Internal pressure (A) and energy (B) profiles as a function of unit cell volume, obtained from (N, V, T) simulations at 300 K. The pressure from simulation is displayed as points with the polynomial fit as a line. Furthermore, we highlight in gray the pressure range for which the structure can exist as two different metastable states. Internal energy is displayed in panel (B) as points compared to free energy, calculated by thermodynamic integration, depicted as a line. Additionally, we feature the volume of op and cp phases as dotted lines.

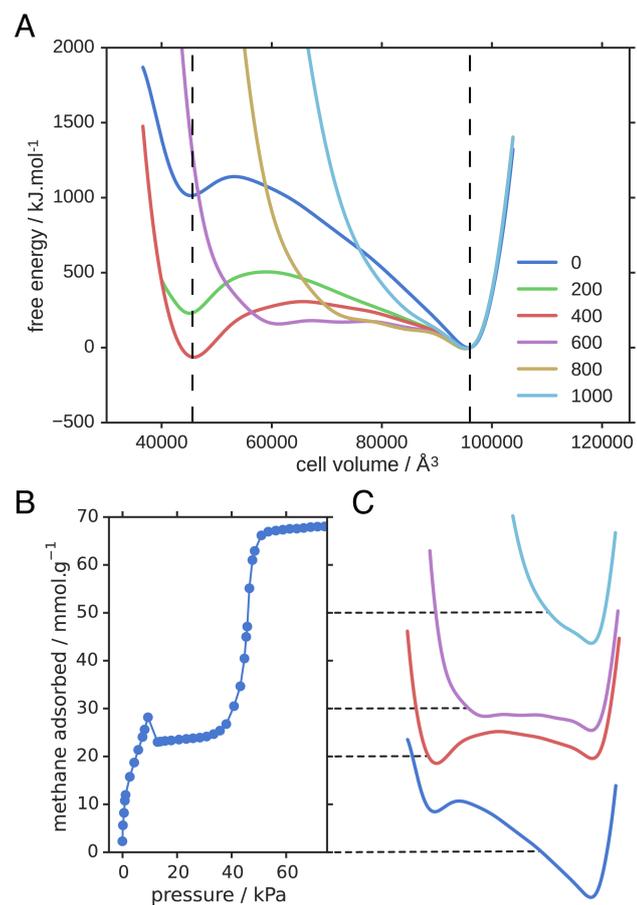


Figure 6: Free energy profiles as a function of unit cell volume (A), obtained from *NVT* simulations at 120 K with increasing amount of methane molecules (molecules per unit cell) and volumes corresponding to the *op* and *cp* phases are displayed as dotted lines. The methane isotherm for DUT-49 at 111 K (B) shown with corresponding free energy profile for a given methane loading (C).

Supporting information for: Origins of Negative Gas Adsorption

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Table S1: Average cell parameters of DUT-49 obtained from a 5 ns (N, P, T) molecular dynamics simulations at 300 K and 1 atm. Parameters found using DFT are displaying in italics.

	DUT-49- <i>op</i>	DUT-49- <i>cp</i>
volume / \AA^3	96000 ± 300 (<i>102000</i>)	45600 ± 400 (<i>47300</i>)
a / \AA	45.8 ± 0.1 (<i>46.72</i>)	35.7 ± 0.4 (<i>36.18</i>)
b / \AA	45.8 ± 0.1 (<i>46.72</i>)	35.7 ± 0.4 (<i>36.18</i>)
c / \AA	45.8 ± 0.1 (<i>46.72</i>)	35.7 ± 0.4 (<i>36.18</i>)
$\alpha / ^\circ$	90.0 ± 0.5 (<i>90.0</i>)	90.0 ± 0.7 (<i>90.0</i>)
$\beta / ^\circ$	90.0 ± 0.5 (<i>90.0</i>)	90.0 ± 0.7 (<i>90.0</i>)
$\gamma / ^\circ$	90.0 ± 0.5 (<i>90.0</i>)	90.0 ± 0.6 (<i>90.0</i>)

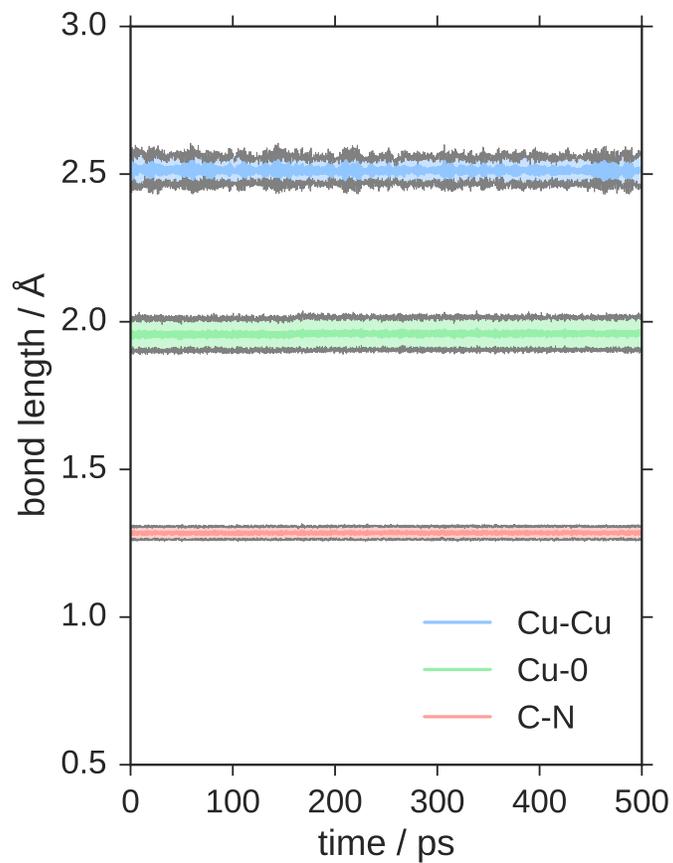


Figure S1: Mean and standard deviation (depicted by a lighter color) of critical bond lengths during the compression period of (N,P,T) simulations with constant isotropic pressure of 60 MPa for 0.5 ns.

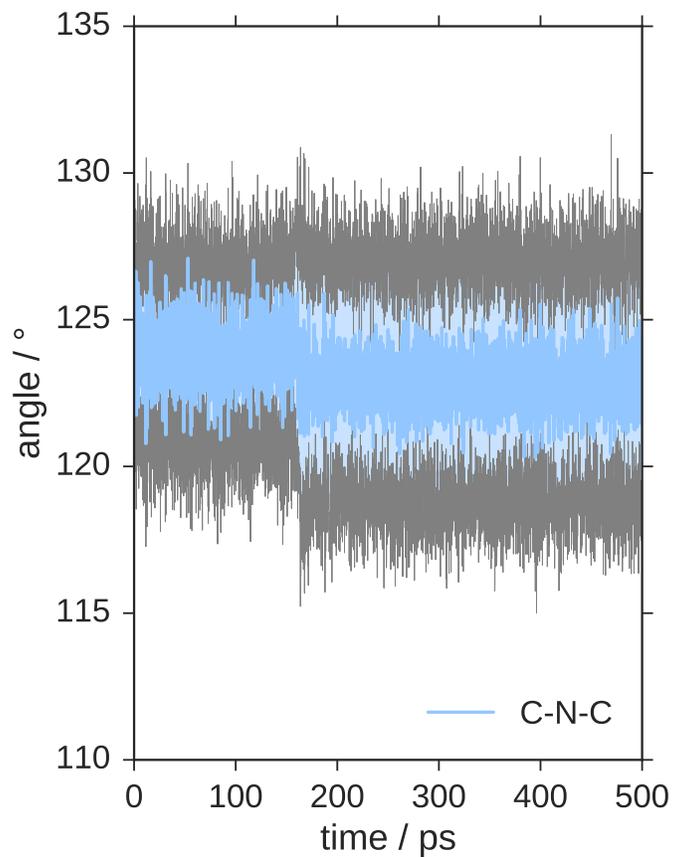


Figure S2: Mean and standard deviation (depicted by a lighter color) of carbazole angles during the compression period of (N,P,T) simulations with constant isotropic pressure of 60 MPa for 0.5 ns.

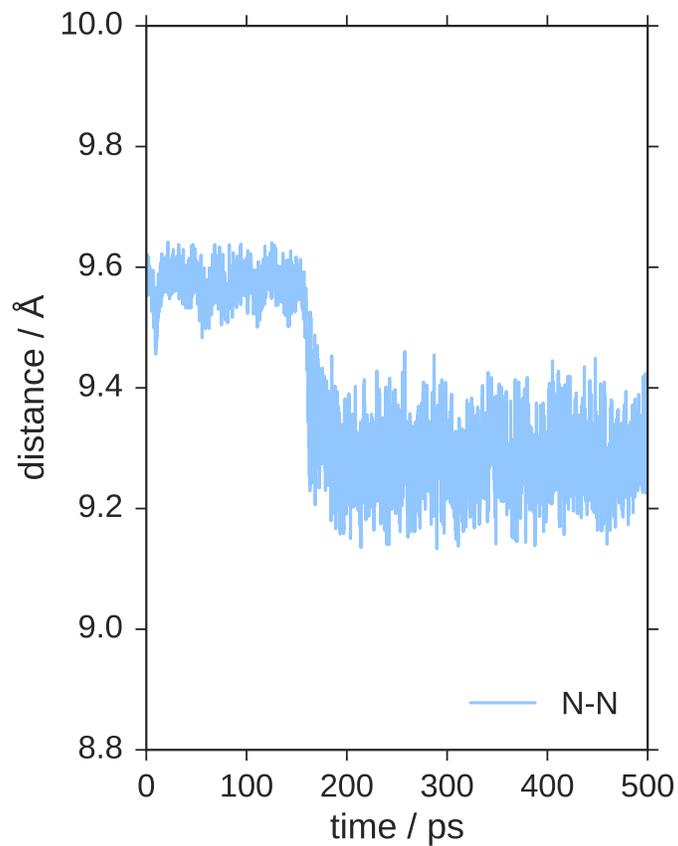


Figure S3: Mean and standard deviation (depicted by a lighter color) of ligand N–N distance during the compression period of (N,P,T) simulations with constant isotropic pressure of 60 MPa for 0.5 ns.

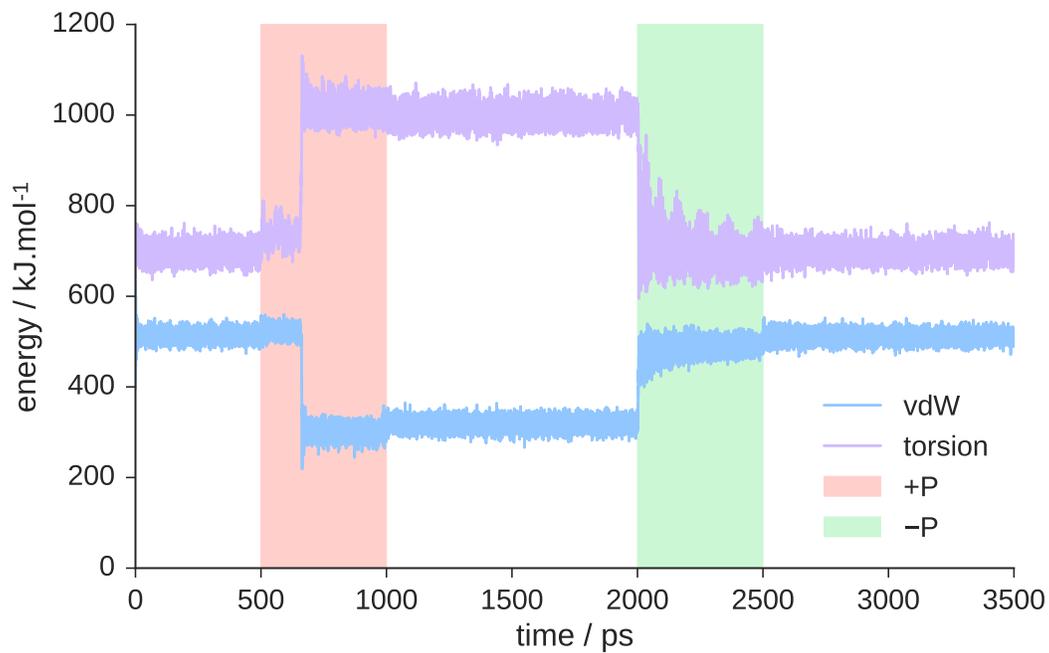


Figure S4: Energy contributions for van der Waals (vdW) and torsion terms during *NPT* simulations with durations of applied pressure for a pressure of ± 60 MPa.

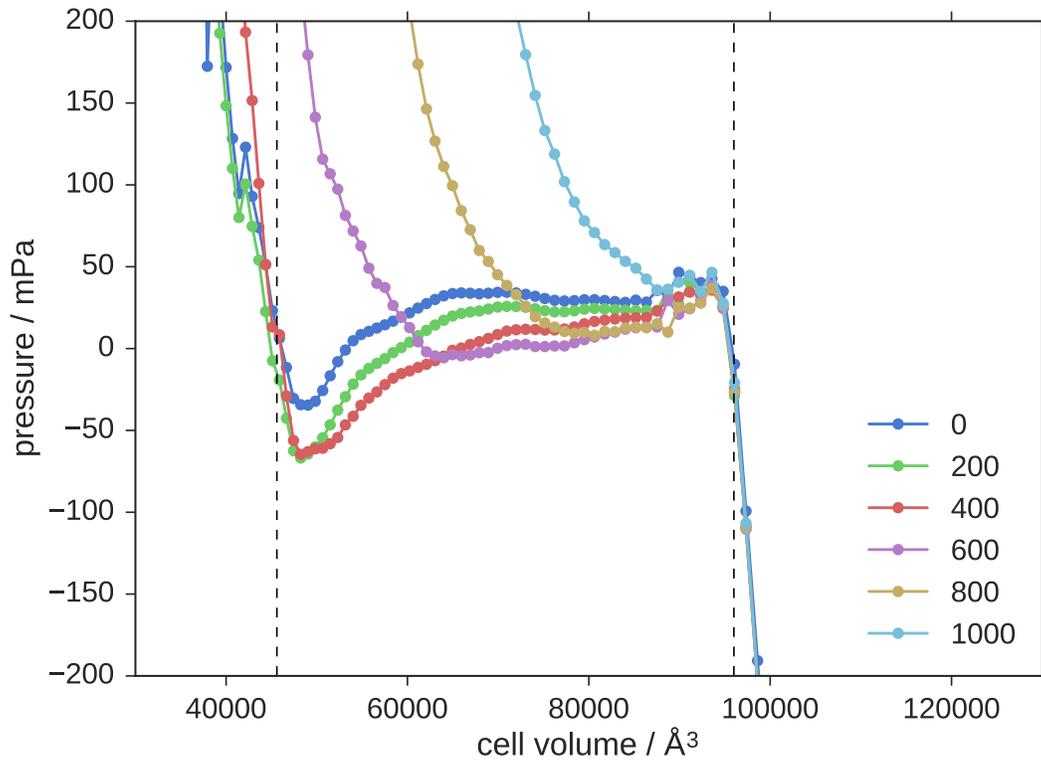


Figure S5: Internal pressure profiles as a function of unit cell volume, obtained from (N, V, T) simulations at 120 K with increasing amount of methane molecules (molecules per unit cell).

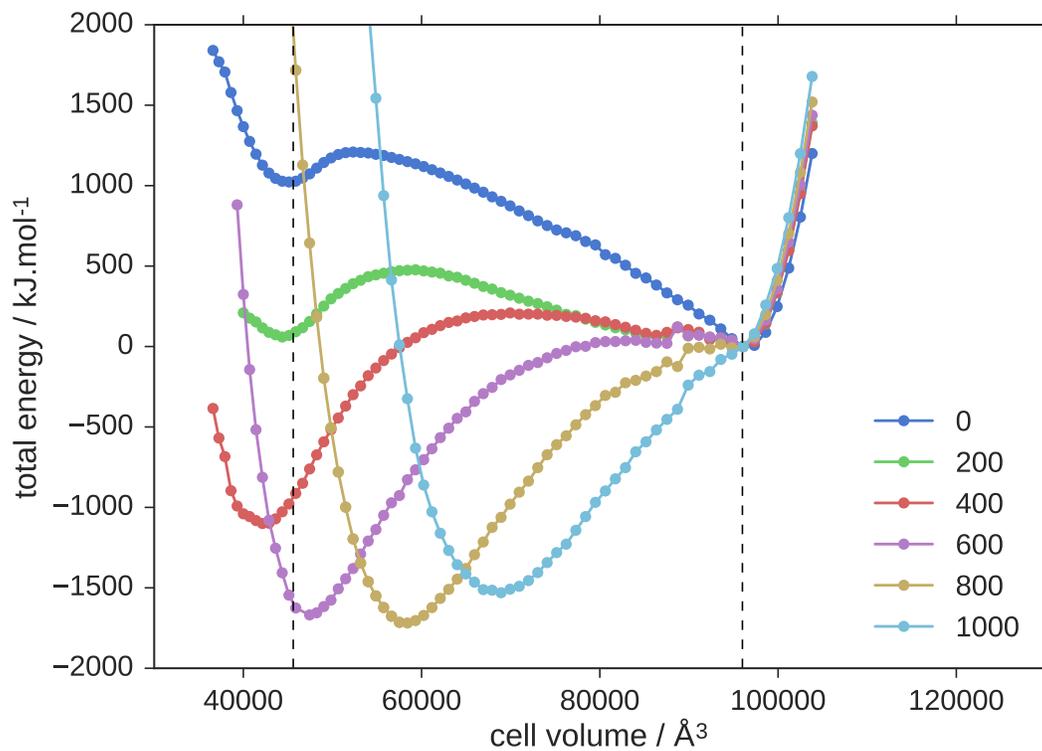


Figure S6: Total energy profiles as a function of unit cell volume, obtained from (N, V, T) simulations at 120 K with increasing amount of methane molecules (molecules per unit cell).