

Supplementary Information

A modified ST-7M transitiometer of the ST-7 model from BGR-Tech was used to obtain PV - diagrams and isobaric heat-capacity of {ZIF-8 + water} molecular spring (MS). The instrument (Fig. 1S) features a differential scanning calorimeter contained in a temperature controlled metallic block which is itself fixed on a special mobile support which allows the whole body (the calorimetric block) to be moved vertically up and down over the calorimetric (measuring and reference) cells firmly fixed on a stand. In the upper position of the calorimetric block the two cells can be accessed to be filled and be tightly closed. After placing the investigated sample into the measuring cell, the two cells are closed with appropriate identical cylindrical covers. These covers ensure to keep the two cells to sustain high pressure and measure the heat flow with the differential calorimetric block. In all experiments all variables (pressure, volume, temperature and calorimetric signal, *i.e.* the heat flow) are registered simultaneously. For details on the ST-7M transitiometer see ref. 11 in the paper. Measurements were performed by controlling precisely the three thermodynamic variables, namely: pressure within ± 0.15 MPa, volume within $\pm 3.3 \times 10^{-4}$ cm³ and a constant temperature within ± 0.01 K.

Sample preparation and experimental procedure are described below. A specific amount of ZIF-8 was introduced into a metallic capsule, which is sealed by a metallic–ceramic porous lid. The approximate weight of the porous powder in the capsule was ~ 1 g. The capsule with powder was thoroughly degassed to about 10^{-2} mbar for 2 – 4 hours. After the degassing procedure, the capsule with powder was filled *in situ* with degassed distilled water through the porous lid. Filling of capsules with water was carried out under vacuum. This procedure guarantees efficient filling of interparticle spaces by water. Next, the capsule containing the MS

is positioned into the measuring cell while an identical capsule just filled with degassed water is positioned into the reference cell. The two cells are each connected to special volumeters with built in bellows which serve to measure volume changes occurring inside the calorimetric cells. Both cells and volumeters were filled before with degassed water. The pressure–volume diagrams for the {ZIF-8 + water} MS were obtained for 2 temperatures (275K and 330K), while the associated volume changes measured by the bellow devices were recorded simultaneously during repeated cycling scans. At each temperature several compression and decompression cycles were realized at 1 MPa/min rate to make sure, of the good reproducibility of measurements. Previously it was verified that such compression rate does not bring any additional effects in comparison with lower (quasi-static) rates. As a matter of fact, measurements under quasi reversible mode are prerequisite for transitiometric runs.

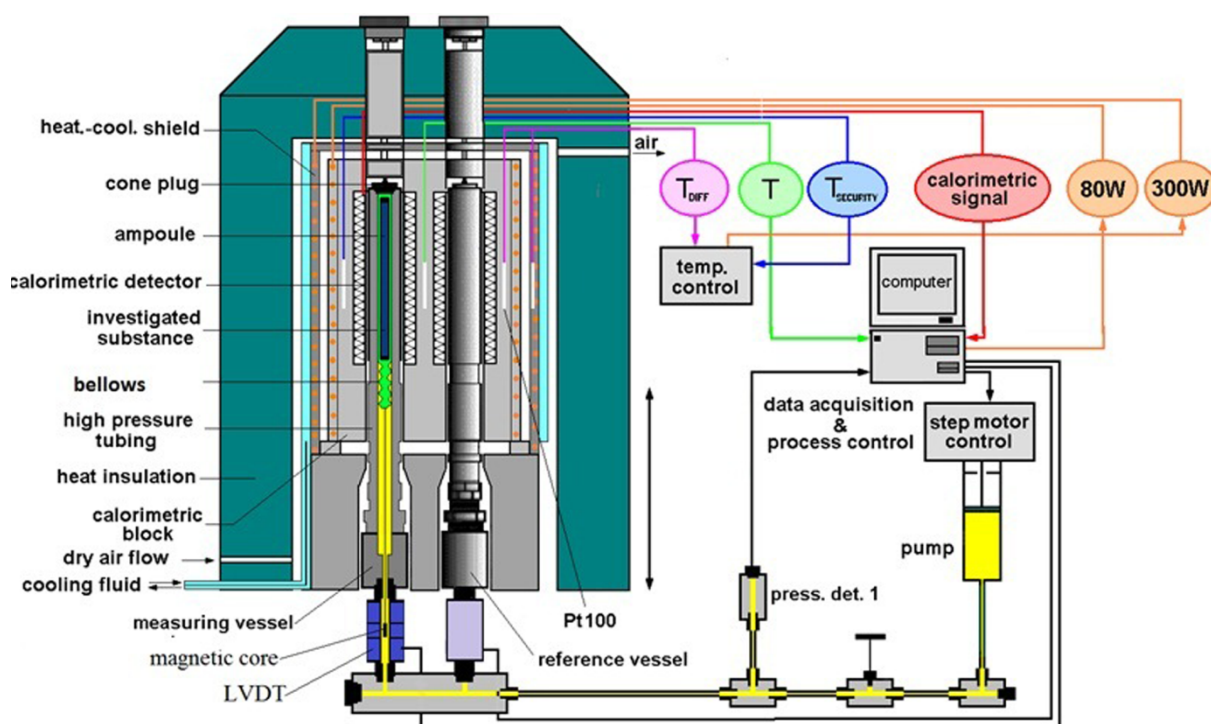


Figure 1S. Transitiometer ST-7M.

For experiments under isobaric conditions constant value of pressure $P_0 = 23.80 \pm 0.15 \text{ MPa}$ was controlled automatically and the temperature scanning rate was

$\left(\frac{\partial T}{\partial t}\right)_P = 5 \cdot 10^{-4} K/s$. Simultaneously the heat flow $\left(\frac{\partial Q}{\partial t}\right)_P$ required to perform programmed temperature change was registered. The value of heat-capacity was then calculated as

$$C_p \equiv \left(\frac{\partial Q}{\partial T}\right)_P = \frac{\left(\frac{\partial Q}{\partial t}\right)_P}{\left(\frac{\partial T}{\partial t}\right)_P}$$

The isothermal compressibility of {ZIF-8 + water} MS is presented on Fig. 2S.

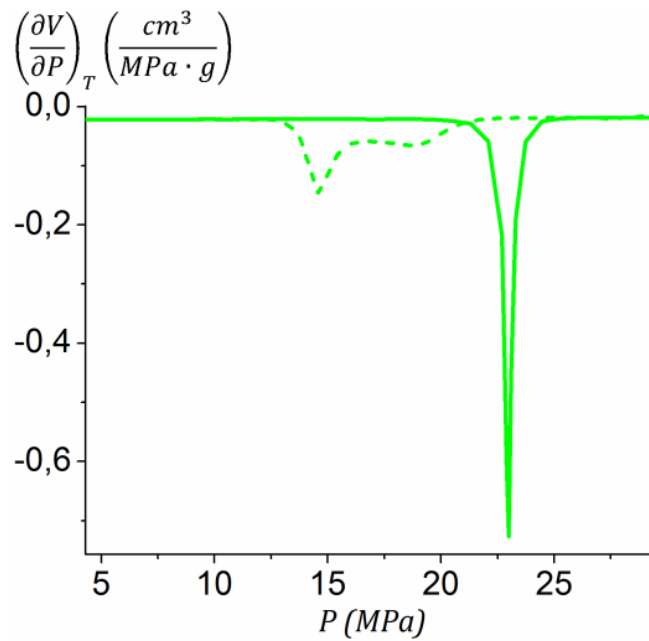


Figure 2S. Pressure dependence of compressibility of {ZIF-8 + water} MS during compression (solid line) – decompression (dashed line) cycle at 275K for a nominal of 1g of ZIF-8