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# 1 Model reduction techniques for quantitative 2 nano-mechanical AFM mode

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10 **Abstract.** A recently developed atomic force microscope (AFM) process, the Peak-  
11 Force Quantitative Nanomechanical Mapping (PF-QNM) mode, allows to probe over a  
12 large spatial region surface topography together with a variety of mechanical properties  
13 (*e.g.* apparent modulus, adhesion, viscosity). The resulting large set of data often  
14 exhibits strong coupling between material response and surface topography. This letter  
15 proposes the use of a proper orthogonal decomposition (POD) technique to analyze  
16 and segment the force-indentation data obtained by the PF-QNM mode in a highly  
17 efficient and robust manner. Two samples illustrate the proposed methodology. In  
18 the first one, low density polyethylene nanopods are deposited on a polystyrene film.  
19 The second is made of carbonyl iron particles embedded in a polydimethylsiloxane  
20 matrix. The proposed POD method permits to seamlessly identify the underlying  
21 phase constituents in both samples and decouple them from the surface topography  
22 by compressing voluminous force-indentation data into a subset with a much lower  
23 dimensionality.

24 *Keywords* : AFM; PeakForce-QNM; Segmentation; Model reduction technique; POD

25  
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## 1. Introduction

Since Scanning Force Microscopy (SFM, aka SPM) was introduced [1], AFM has evolved into one of the most powerful tools for surface characterization [2]. Various new AFM modes has been proposed to provide local material properties together with topography with a high scanning rate (*e.g.*, Tapping Mode [3], Pulse force Mode [4, 5], Contact Resonance-AFM [6] and etc). Peak-Force Quantitative Nanomechanical Mapping (PF-QNM) AFM mode has been introduced [7] as a new extension of previous Pulse Force AFM mode, aiming to robustly explore simultaneously various nanoscale mechanical properties [8–11]. By monitoring the instantaneous deflection of the cantilever, a continuous feedback loop is implemented to control the force between the tip and sample [12, 13]. Force-indentation curves are generated separately for each tip oscillation (pixel by pixel) inside the region of interest (ROI), allowing to probe not only morphological properties (*e.g.* surface topography) but also various material mechanical properties such as Young’s modulus, visco-elasticity, adhesion, or any indentation related properties [14–16].

In a PF-QNM analysis or any other type of micro/nano-indentation process, the measured force-indentation data involve the combined effect of sample topography, physical and chemical material properties [17–19], as well as the effective contact area between tip and sample. For most intrinsically hard materials (*e.g.* metals and ceramics), both the indentation size effect has been well investigated [20–24] and data analysis tools to estimate a reliable Young modulus has been established [25, 26].

On the contrary, the lack of reliable nonlinear elastic contact models frequently compels the (inappropriate) use of Hertzian or Sneddon models to estimate the local apparent modulus and likely contributes to inconsistencies associated with the results of AFM measurements [27, 28]. As a result, the mere use of the sole apparent modulus is insufficient to properly segment the phases in heterogeneous samples in a PF-QNM mode [14, 27]. By contrast, use of the entire spatial and temporal force-indentation information may prove highly inefficient due to voluminous and overlapping data-sets that cannot be segmented properly and consequently lead to multiple fake material phases as a result of user-dependent segmentation processing.

From a data-mining perspective, the multi-dimensional character of the data does not allow for an intuitive and rigorous analysis [29], as compared to more classical two- and three-dimensional data spaces. In order to overcome the multi-dimensional and complex nature of the raw data obtained in a classical PF-QNM mode, it is proposed in this letter the use of a model reduction analysis such as the Proper Orthogonal Decomposition technique (POD [30] aka SVD [31] or PCA [32]). This technique allows to reorganize the data hierarchically, so that a mere truncation is a natural way to focus on the dominant features of the data-set, leaving aside higher-order information that contribute only weakly to the resulting force-indentation response at a given pixel. Furthermore, the truncation order is a choice that can be tuned if needed. This allows to clearly identify the underlying phases of the heterogeneous material and even decouple

68 them from the surface topography, which usually interferes with the measured force  
 69 response. In this view, the POD truncation is an effective method to convert the  
 70 voluminous data-set into a subset with a much lower dimensionality and first-order  
 71 information, where relevant features can be easily observed. Note however that the  
 72 proposed approach is agnostic with respect to the physics of data. This makes the  
 73 method highly versatile as no prior knowledge is encoded in the method, yet, it calls  
 74 for a final physical, chemical and/or mechanical interpretation of the segmented data.  
 75 This latter part is beyond the scope of the present letter and is left for a future study.

76 The efficiency of the proposed methodology is illustrated by two different  
 77 heterogeneous samples. The first one consists of low density polyethylene (LDPE)  
 78 canonical well-shaped disks, with no overlap, deposited on a polystyrene (PS) matrix,  
 79 and is used as a patch test. The second sample comprises, in turn, hard micron-  
 80 sized carbonyl-iron particles (CIP) embedded into a polydimethylsiloxane (PDMS)  
 81 matrix [33–36] leading to strong topography variations and non-trivial force-indentation  
 82 spatial response.

## 83 2. PeakForce QNM mode

84 The experimental characteristics and output of the AFM PF-QNM mode are briefly  
 85 described in Fig. 1. The laser spot is focused on the surface of the cantilever beam  
 86 (Fig. 1a) and the associated probe measures the laser shifting voltage (LSV) over  
 87 time,  $\delta V(\mathbf{x}, t)$  at a given pixel on the surface described by the in-plane position  
 88 vector  $\mathbf{x} = (x, y)$ . After a proper calibration process (usually performed on a non-  
 89 deformable sapphire sample), the bending stiffness of the cantilever  $\kappa$  and the sensitivity  
 90 of the cantilever deflection  $\gamma$  are estimated assuming a *linear elastic, pure-bending*  
 91 response. This allows to directly associate the LSV measurement to the reaction force by  
 92  $F(\mathbf{x}, t) = \kappa \delta V(\mathbf{x}, t)$  (Fig. 1b) and the cantilever deflection as  $d_{\text{df}} = \gamma \delta V(\mathbf{x}, t)$  (Fig. 1c).  
 93 The actual indentation depth  $\delta(\mathbf{x}, t)$  of the cantilever tip is given as the difference of  
 94 the prescribed vertical displacement of the cantilever  $Z$  (Fig. 1d) and the cantilever  
 95 deflection as  $d_{\text{df}}$ ,  $\delta(\mathbf{x}, t) = Z - d_{\text{df}}$ .

96 Use of  $\delta$ , instead of  $Z$  or of time  $t$ , allows for the influence of topography to be erased  
 97 for the most part. Fig. 1e shows a representative force-penetration,  $F - \delta$ , response at a  
 98 fixed position (pixel)  $\mathbf{x}$ . The paths A→B→C→D (blue line) and D→E→F (red line)  
 99 correspond to the loading and unloading response, respectively.

100 The entire  $F - \delta$  response may then be divided in four main regimes (Fig. 1e):

101 – **Regime I: A→B→C**. As the tip approaches the surface of the specimen, an  
 102 unstable jump towards contact occurs. The first force minimum during loading at  
 103 B is used as a conventional *definition* of contact, and thus as an estimate of surface  
 104 topography. However, because of the intrinsically unstable character of this “snap-  
 105 in” and its associated hysteresis [37], this commonly adopted definition appears to be  
 106 delicate, and may intermingle topography with surface force gradients. An alternative  
 107 more rigorous definition of topography may be obtained with regard to point C, where

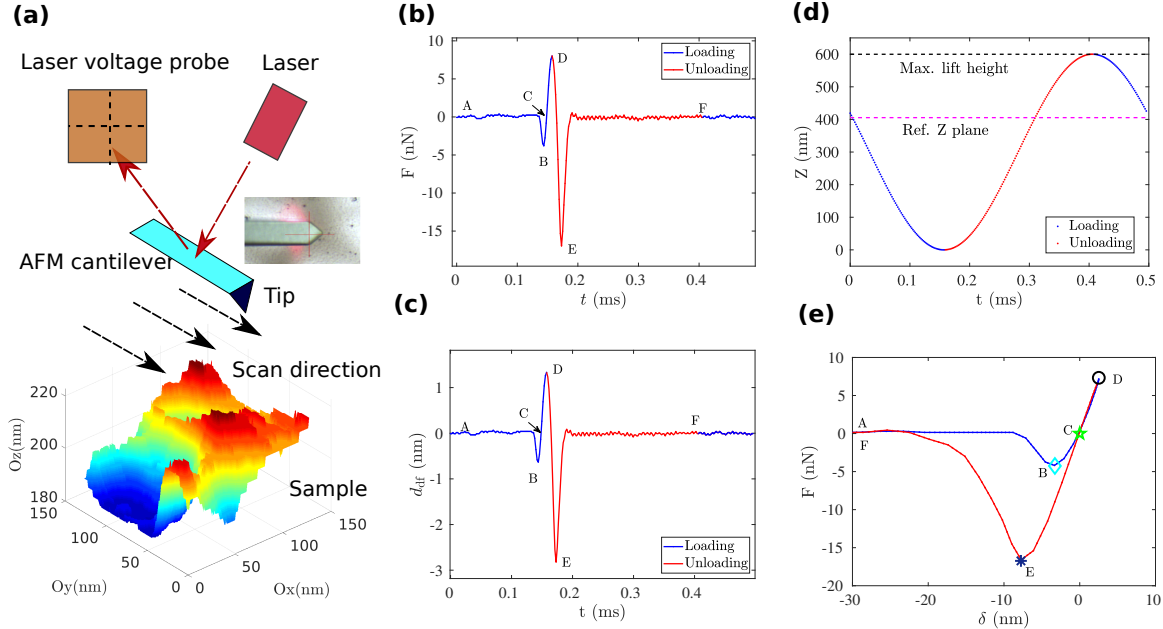


Figure 1: PeakForce QNM AFM mode. (a) AFM PeakForce QNM mode: a prescribed displacement loading is repeated in every pixel along the scanning direction; a laser beam reflected by AFM cantilever, is measured by a photo-diode delivering a laser shifting voltage (LSV), which can be converted in cantilever tip position and force at each instant in time  $t$ . (b) The deflection force  $F$  vs. time  $t$ , (c) cantilever deflection  $d_{df}$  vs. time  $t$ , (d) total vertical displacement of the cantilever  $Z$  vs. time  $t$ , (e) deflection force  $F$  vs. actual indentation depth  $\delta = Z - d_{df}$ . The markers denote the different regimes discussed in the main text.

108 the tip is in contact with the surface exerting a zero overall applied force. Thus the  
 109 surface elevation  $\delta_e(\mathbf{x})$  at a spatial point  $\mathbf{x}$  is obtained by the implicit equation

$$110 \quad F(\mathbf{x}, \delta_e(\mathbf{x})) = 0. \quad (1)$$

111 – Regime II: C→D. As the cantilever is pushed towards the surface, the force turns  
 112 from attractive (before point C) to repulsive (after point C) and reaches a maximum at  
 113 point D.

114 – Regime III: D→E. The tip is then withdrawn (unloading), and the response is  
 115 that of a (visco)-elastic adhesive contact. Adhesion can be characterized through the  
 116 pull-out force  $F$  reached at point E in the  $F - \delta$  curve (dark blue star symbol).

117 – Regime IV: E→F. Complete retraction of the tip is mainly dominated by the  
 118 mechanical instability of tip detachment from the surface, similar to Regime I, but with  
 119 a higher amplitude because of adhesion.

120 One often assumes that the sample remains purely elastic during the unloading cycle  
 121 D→E, so that an effective apparent Young’s modulus can be estimated, using either a  
 122 Hertz or a Sneddon contact model. Nonetheless, if nonlinear and/or viscous effects are  
 123 present, this analysis can lead to erroneous results, as is the case here especially in the  
 124 second PDMS-CIP sample.

### 125 3. Proper Orthogonal Decomposition

126 This section discusses in some detail the proper orthogonal decomposition (POD)  
 127 analysis used to analyze the force-indentation data obtained from the PF-QNM AFM  
 128 mode. Initially introduced in Ref. [38] to study turbulence, the POD is a powerful  
 129 and elegant method for data analysis aimed at obtaining low-dimensional approximate  
 130 descriptions of a large data-set.

131 Specifically, in the present work, the force-indentation response is collected in a  
 132 matrix form  $\mathbf{F}(\mathbf{x}_i, \delta_j)$  written in index notation as  $F_{ij}$ . This matrix is sampled at  
 133 each pixel position,  $\mathbf{x}_i$ , ( $i = 1, \dots, N_x$  with  $N_x$  denoting the number of pixels) and each  
 134 indentation depth,  $\delta_j$  ( $j = 1, \dots, N_\delta$  with  $N_\delta$  denoting the dimension of the indentation  
 135 discretization). It should be noted here that linear interpolation between subsequent  $\delta_j$   
 136 is required in general to obtain intermediate data necessary for the subsequent processes.

The POD analysis allows then to separate the matrix  $\mathbf{F}$  into a set of orthonormal  
 basis vectors (the POD modes) for representing a given data in the form

$$\mathbf{F}(\mathbf{x}, \delta) = \sum_{n=1}^{N_\delta} \lambda^{(n)} \mathbf{U}^{(n)}(\mathbf{x}) \mathbf{W}^{(n)}(\delta), \quad \text{or} \quad F_{ij} \equiv \sum_{n=1}^{N_\delta} \lambda^{(n)} U_i^{(n)} W_j^{(n)}. \quad (2)$$

137 Here,  $\mathbf{W}^{(n)} \in \mathbb{R}^{N_\delta}$  represents the elementary force-indentation mode (normalized as  
 138  $\|\mathbf{W}^{(n)}\| = 1$ †),  $\mathbf{U}^{(n)} \in \mathbb{R}^{N_x}$  is the spatial modulation of this elementary response  
 139 (normalized as  $\|\mathbf{U}^{(n)}\| = 1$ ) and  $\lambda^{(n)}$  is a global modal amplitude. At this stage, no  
 140 approximation is involved, and for all data series  $\mathbf{F}(\mathbf{x}, \delta)$ , such an exact space-indentation  
 141 decomposition always exists (but is not unique).

Then, one may easily show that both the spatial and the force modes are orthogonal,  
 i.e.,

$$\mathbf{U}^{(n)} \cdot \mathbf{U}^{(m)} = \mathbf{W}^{(n)} \cdot \mathbf{W}^{(m)} = \delta^{(nm)} \quad (3)$$

with  $\delta^{(nm)} = 1$  if  $n = m$  and 0 otherwise. From the orthonormality conditions, the  
 following relations can be readily derived

$$\lambda^{(n)} \mathbf{U}^{(n)} = \mathbf{F} \mathbf{W}^{(n)} \quad (4)$$

$$\lambda^{(n)} \mathbf{W}^{(n)} = \mathbf{U}^{(n)} \mathbf{F} \quad (5)$$

Finally, the eigenvalues can be used to evaluate the relative “energy”,  $\tau_n$ , of the  
 $n$ -th POD mode as

$$\tau_n = \frac{(\lambda^{(n)})^2}{\sum_m (\lambda^{(m)})^2}. \quad (6)$$

142 The most important property of the POD (that can be chosen as a definition) is  
 143 the fact that modes can be ordered in terms of their significance for representing the

† We use a standard definition of the Euclidean vector norm  $\|\mathbf{A}\| = \sqrt{\mathbf{A} \cdot \mathbf{A}}$ , where  $\mathbf{A}$  is a vector of  
 any finite dimension.

144 data. Then, one may retain only a very small number of those modes to approximate  
 145 the original response. Both  $\mathbf{U}^{(n)}$  and  $\mathbf{W}^{(n)}$  as well as the number,  $N \ll N_\delta$ , of those  
 146 retained modes are determined so that the norm of the difference between left and right  
 147 hand side terms of Eq. (2) is minimized for any choice of  $N$ .

From the algorithmic point of view,  $\lambda^{(n)}$  appear as eigenvalues sorted in descending  
 order, whereas either  $\mathbf{U}^{(n)}$  or  $\mathbf{W}^{(n)}$  are the associated eigenvectors. Hence, the  
 truncation of the above relation (Eq. 2) after the first  $N < N_\delta$  modes,

$$\tilde{\mathbf{F}}_N \equiv \sum_{n=1}^N \lambda^{(n)} \mathbf{U}^{(n)}(\mathbf{x}) \mathbf{W}^{(n)}(\delta), \quad (7)$$

148 provides the best approximation of the original data in a least squares sense for a given  
 149 number of modes. As a result, the POD offers a simple way of compressing the data to  
 150 a low dimensional space, while guaranteeing the optimality (or minimal loss) of such an  
 151 approximation.

To estimate the accuracy of the approximate description obtained by the POD  
 truncation, conventionally the residual  $\rho_i$  at every spatial position  $\mathbf{x}_i$  can be computed  
 as

$$\rho_i(\mathbf{x}_i) \equiv \rho_i = \frac{\sum_{j=1}^{N_\delta} (F_{ij} - (\tilde{F}_N)_{ij})^2}{\sum_{j=1}^{N_\delta} (F_{ij})^2}, \quad i = 1, \dots, N_x. \quad (8)$$

152

#### 153 4. Patch-test: LDPE nano deposits on a PS film

154 First, a sample made from low density polyethylene (LPDE) well-separated nanopods  
 155 deposited on a polystyrene (PS) substrate is considered (Fig. 2)§. This sample serves  
 156 as a patch test in our work since it is commonly used to calibrate AFM tips (RTESPA-  
 157 150 type). For the patch-test, a ROI area of  $S = 5 \times 5 \mu\text{m}^2$  is scanned with a spatial  
 158 resolution of  $64 \times 64$  points and a frequency of acquisition 2 kHz.

159 Fig. 2b shows the force-indentation response for twenty random selected pixels  
 160 inside the ROI. It is clear that the corresponding force-indentation response can be  
 161 divided into two main data-groups: the first one exhibits a stiff response with low  
 162 adhesion and negligible viscosity, whereas the second one shows a softer response and  
 163 with high adhesion and viscosity (as indicated by the hysteresis during unloading).

164 It is essential to point out that even if the PF-QNM mode is controlled to reach a  
 165 predefined maximum contact force, this is in practice unattainable, as the scan frequency  
 166 and the complex topography prevent this condition from being accurately satisfied. As  
 167 a consequence, neither the force range nor the indentation interval are kept constant

§ The SEM image does not correspond exactly to the area analyzed by the AFM. Yet, it validates qualitatively the AFM results.



168 from pixel to pixel, and thus, for a fair comparison of responses at different pixels, one  
 169 must crop the raw recorded data to a well defined indentation or force level.

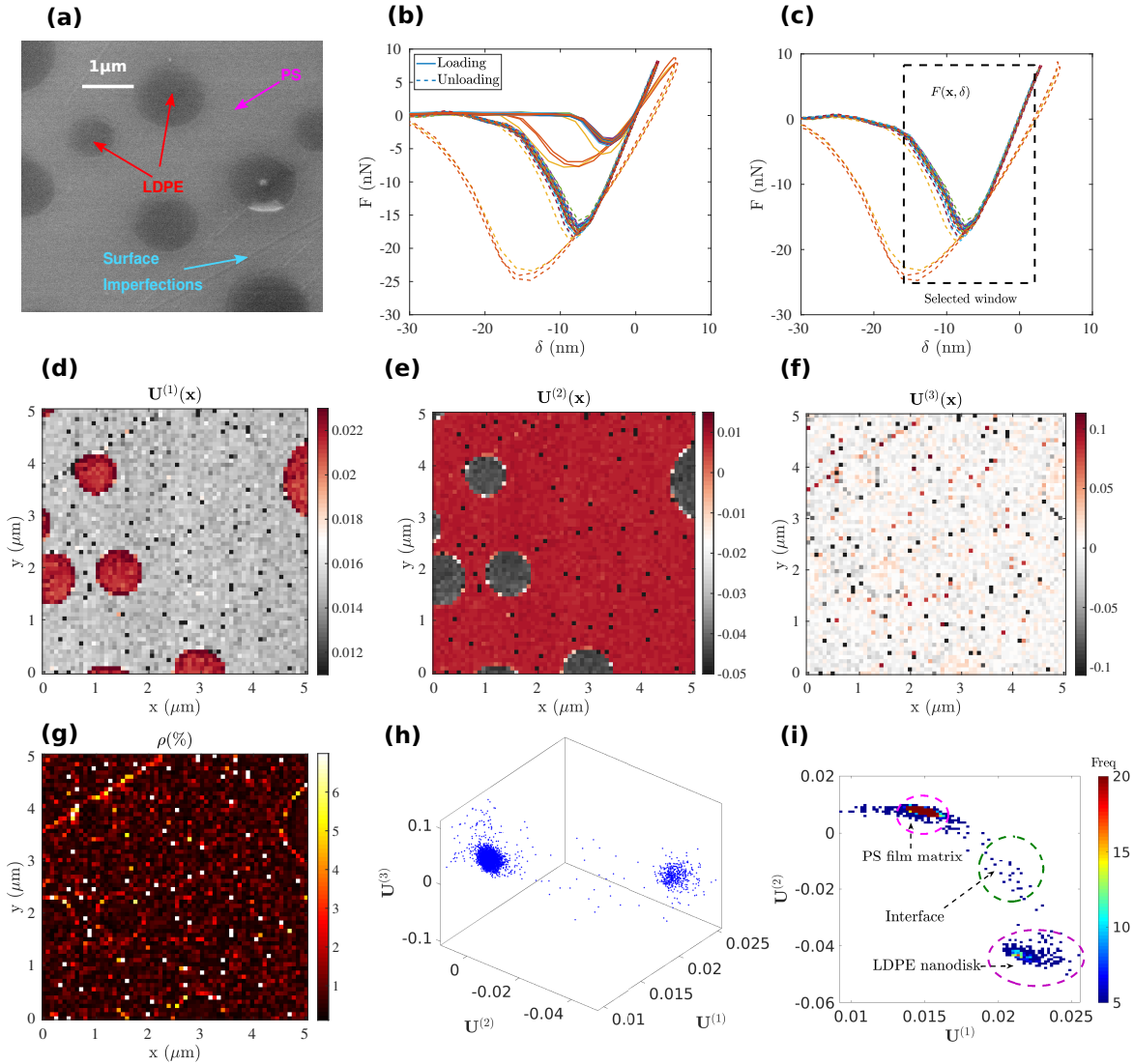


Figure 2: (a) SEM image showing LDPE nanodisks deposited on PS substrate and surface imperfections. (b) Arbitrarily selected force-indentation response at various pixels (continuous lines represent tip approach and dashed lines tip retraction). (b) Force-indentation curve during retraction; the rectangle indicates the region selected for POD analysis. (d) First POD mode spatial mode revealing the phases (e) Second POD mode revealing more subtle information such as PS-LPDE interfaces. (c) Third POD mode showing higher order features related to surface roughness. (g) Residual error resulting by keeping only the first three modes to describe the force-indentation response at each pixel. (h) Subspace generated by the first three POD modes  $[\mathbf{U}^{(1)}; \mathbf{U}^{(2)}; \mathbf{U}^{(3)}]$ . (i) Contour of the frequency of points in the subspace  $[\mathbf{U}^{(1)}, \mathbf{U}^{(2)}]$ .

170 In this regard, for the patch test, the force-indentation response is analyzed  
 171 only during unloading, i.e., Regime III, as shown by the cropping window in Fig. 2c  
 172 (approximately  $-15 \text{ nm} \lesssim \delta \lesssim 5 \text{ nm}$ . The contact response is initially (visco)elastic



173 and subsequently adhesive between the tip and the sample. This implies that our phase  
 174 segmentation is done for this specific part of the  $F - \delta$  response and has to be interpreted  
 175 as such.

176 Subsequently, the cropped force-indentation data points are decomposed into  $N$   
 177 POD (proper orthogonal decomposition) modes as described by Eq. (7). We show next  
 178 that the first few POD modes can reproduce most of the complete  $F - \delta$  response by  
 179 evaluating the relative power of each POD mode  $\tau_n$  in the original data is evaluated via  
 180 Eq. (8).

181 Fig. 2(d-f) shows the first three POD spatial modes  $\mathbf{U}^{(n)}(\mathbf{x}_i), n \leq 3$ , ranked  
 182 from higher to lower value of  $\tau_n$ . These first three POD modes represent 96% of  
 183 the original measured  $F - \delta$  response, leading respectively to the values,  $\tau_1 = 0.75$ ,  
 184  $\tau_2 = 0.17$ , and  $\tau_3 = 0.04$ . The first POD mode  $\mathbf{U}^{(1)}$  captures remarkably well the phase  
 185 distributions (PS in gray and LDPE in light red in Fig. 2d) as the primary information  
 186 of the mechanical response. The second mode,  $\mathbf{U}^{(2)}$ , (Fig. 2e) reveals the next level of  
 187 information. In particular, light gray areas at the PS-LPDE interfaces indicates that  
 188 the mechanical properties in those regions are somewhat different. Finally, the third  
 189 mode  $\mathbf{U}^{(3)}$  describes even higher order information that do not affect the first order  
 190 effects such as the contact laws and material stiffness (Fig. 2f). For instance, the  $\mathbf{U}^{(3)}$   
 191 map reveals regions with steep slopes, such as a scratch at the north-west side, which  
 192 correlates well with similar defects revealed in the SEM image (Fig. 2a).

193 The contributions of higher POD modes,  $n > N$ , are negligible as compared to the  
 194 first three ones and lead mostly to a pure noise map. In this view, the residual  $\rho$  can  
 195 be computed, to highlight pixels where the mechanical response is not very accurately  
 196 accounted for with the number of POD modes used (Fig. 2g). For a more quantitative  
 197 analysis, Fig. 2h shows the distribution of data in the subspace  $[\mathbf{U}^{(1)}; \mathbf{U}^{(2)}; \mathbf{U}^{(3)}]$ , where  
 198 pixels are grouped into clusters. This allows the segmentation of the different phases and  
 199 the identification of one or more interfacial regions. Focusing further in the subspace  
 200  $[\mathbf{U}^{(1)}; \mathbf{U}^{(2)}]$  (Fig. 2i), a 2D-histogram shows the statistical frequency of points having a  
 201 given value of  $\mathbf{U}^{(1)}$  and  $\mathbf{U}^{(2)}$ . Two main phases characterized by their mean response and  
 202 deviations are very clearly highlighted making mechanically-based segmentation quite  
 203 simple.

## 204 5. Carbon-Iron particles with PDMS binder

205 The second analyzed sample is a composite material consisting of a polymer matrix  
 206 (PDMS) and mechanically stiff, fairly spherical carbonyl-iron particles (CIP) with mean  
 207 radius of about  $\sim 3 \mu\text{m}$ . The results from the built-in QNM results are first shown  
 208 in Fig. 3 to reveal the complexity of the analyzed sample. Subsequently, in Fig. 4, we  
 209 analyze the data using the proposed POD method.

210 As seen in Fig. 3a obtained by SEM, the white spots represent the reflections from  
 211 the CIP, whereas the surface of the composite material is marked by multiple line defects.  
 212 For the AFM analysis, a surface of  $50 \mu\text{m}^2$  is scanned using the PF-QNM mode with a

213 definition of  $128 \times 128$  points, and a frequency of 2 kHz. The scanned region is selected  
 214 intentionally such that one of the surface imperfections is present in the ROI.

215 As easily observed in Fig. 3b, and unlike the previous ideal patch-test, the variation  
 216 of the force-indentation curves exhibits a continuous pattern and a marked presence of  
 217 viscosity and adhesive behavior. As a consequence, it is extremely difficult to segment  
 218 and identify the underlying phases via a direct pixel-to-pixel analysis. In particular,  
 219 as highlighted in Fig. 3c, a marked surface imperfection is observed inside the ROI  
 220 (highlighted in dark color expanding from south-west to north-east). Due to the sharp  
 221 change in topography and difference in effective contact surface, at these locations,  
 222 both the maximum of indentation depth and adhesion are quite different than either  
 223 the PDMS or the CIP response, and thus it is likely to be misinterpreted as a third  
 224 phase. In the following, the results obtained from our POD proposed approach will be  
 225 shown and compared with the standard PF-QNM ones.

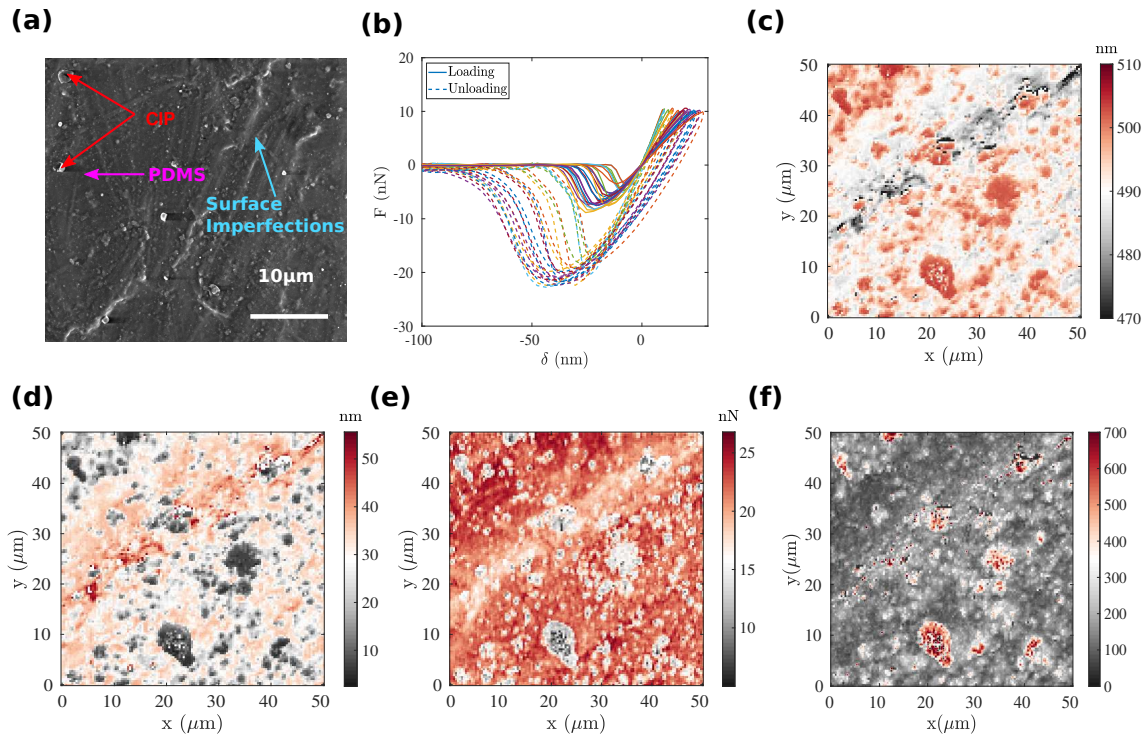


Figure 3: (a) SEM image showing carbonyl iron particles (CIP) embedded in a PDMS matrix, and surface imperfections. (b) Arbitrarily selected force-indentation response at various pixels (continuous lines represent tip approach and dashed lines tip retraction). (c) Topography map using our proposed definition; (d)-(f) Bruker's PF-QNM built-in results maximum indentation; (d) Maximum Indentation (e) Adhesion (f) Apparent modulus using Sneddon model;

226 Following the same POD procedure presented in the previous section, a window is  
 227 selected in the unloading Regime III (Fig. 4a) with  $\delta$  ranging from  $\sim -45$  nm to  $\sim 10$  nm.  
 228 In this initial data-set, after the POD analysis, the first three modes are retained, as  
 229 shown in Fig. 4(b-d). Their contribution amounts to  $\tau_1 = 0.91 > \tau_2 = 0.04 > \tau_3 = 0.03$ ,  
 230 respectively, describing approximately 98% of the power of the original  $F - \delta$  data.

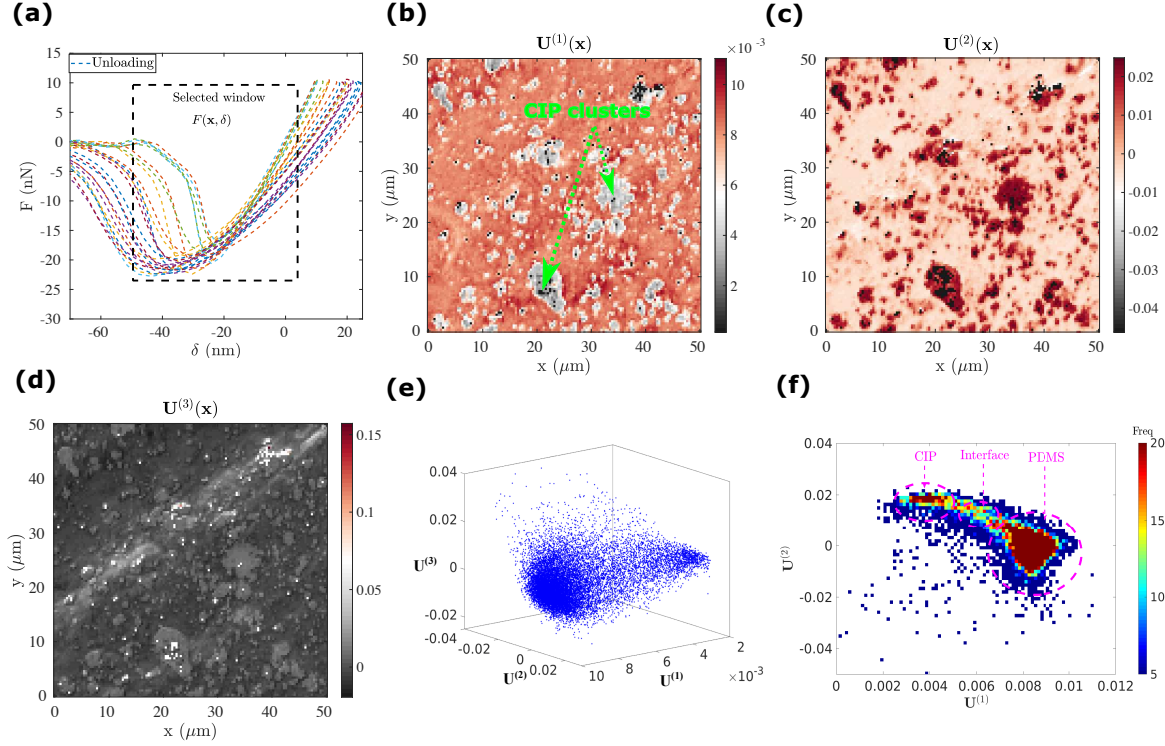


Figure 4: (a) Force-indentation curve during retraction; the rectangle indicates the region selected for POD analysis. (b)-(c) First two POD mode spatial modes revealing clearly the CIP-PDMS phases (d) Third POD mode showing higher order features related to surface roughness.(e) Subspace generated by the first three POD modes  $[\mathbf{U}^{(1)}; \mathbf{U}^{(2)}; \mathbf{U}^{(3)}]$ . (f) 2D histogram of amplitudes in the subspace  $[\mathbf{U}^{(1)}, \mathbf{U}^{(2)}]$ .

231 Remarkably, despite the continuous pattern in the  $F - \delta$  responses (Fig. 4a), the  
 232 first mode  $\mathbf{U}^{(1)}$  (Fig. 4b) reveals the presence of the PDMS matrix (in red) contrasting  
 233 with the much smaller amplitude of the stiff CIP phase (in white). In particular, we  
 234 observe a pronounced clustering of CIP particles in at least four regions that exceed a  
 235 side length of 10  $\mu\text{m}$  (i.e., 3-4 times the radius if the particle) due to aggregation during  
 236 the sample fabrication. Fig. 4b illustrates the strength of the AFM-POD analysis as  
 237 compared with the SEM imaging, wherein such delicate features are much more difficult  
 238 to obtain.

239 The second mode (Fig. 4c) in the present case does not exhibit substantially  
 240 different features than the first one. In fact, one may note that the CIP particles  
 241 now have a much larger weight than the soft matrix, *i.e.* opposite to the case of the first  
 242 mode. With our proposed algorithm, the rough surface topography does not appear to  
 243 bias the phase contrast seen in Fig. 4b and c. By contrast, the surface topography is  
 244 mingled with the phase contrast in all the different Bruker outputs in Fig. 3. Thus, it  
 245 may be concluded that in the present examples, the POD analysis is a trustworthy and  
 246 efficient method for phase segmentation.

247 Finally, the third mode (Fig. 4d) reveals the next order of information, this time  
 248 highlighting the aforementioned topographical defect (light white color) ranging from

south-west to north-east. In the literature, the influence of topography on apparent  
 adhesion has been intensively studied. A sharp variation in surface curvature often leads  
 to a decrease in adhesion for the same material [39]. This observation is consistent with  
 the results reported here as well as those processed by the Bruker AFM software, in spite  
 of the fact that the first modes were observed to be independent of topography. Hence,  
 the POD analysis appears to be an efficient method for rearranging hierarchically and  
 separately different features in PF-QNM AFM data (phase, topography) according to  
 their contribution in the mechanical signal, allowing analysts to describe each individual  
 aspects or their combination altogether.

Focusing, next, on the reduced subspace  $[\mathbf{U}^{(1)}; \mathbf{U}^{(2)}; \mathbf{U}^{(3)}]$  allows to reveal the  
 continuous distribution of the data (Fig. 4e). Given that topography is almost  
 entirely suppressed in the first two POD modes, the subspace  $[\mathbf{U}^{(1)}; \mathbf{U}^{(2)}]$ , (Fig. 4f),  
 becomes a natural “best-candidate” for the purpose of phase segmentation. Two distinct  
 peaks, corresponding to the two main phases, i.e, PDMS and CIP can be observed.  
 However, the scatter of points and the overlap of the two domains suggests in this  
 case that the transition (in terms of apparent mechanical properties) is progressive. It  
 may be speculated that particles buried at different depth beneath the surface may be  
 responsible for this observation.

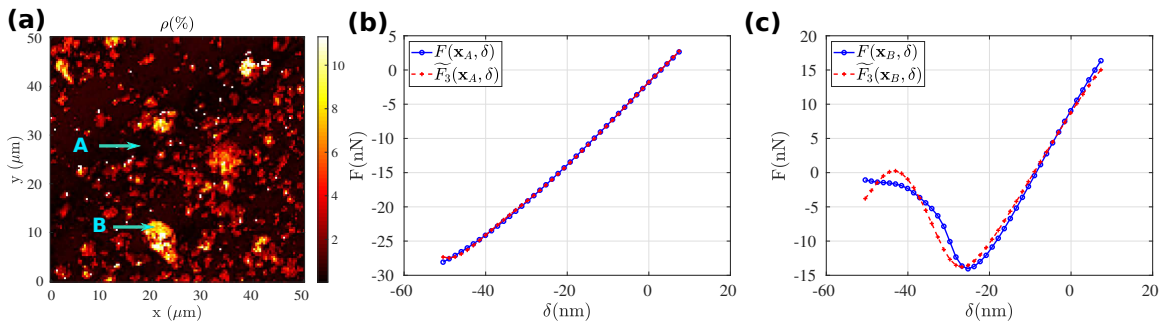


Figure 5: Uncertainty(residual) of reconstruction using the first three POD modes: (a) The residual map ; (b) Comparison between the initial force-indentation curve (plotted in dot blue) and reconstructed curve (plotted in red) at point A ( $\rho(\mathbf{x}_A) \simeq 1\%$ ); (c) Comparison between the initial force-indentation curve (plotted in dot blue) and reconstructed curve (plotted in red) at point B ( $\rho(\mathbf{x}_B) \simeq 10\%$ )

Finally, in order to assess the accuracy of the POD reconstruction, we show in  
 Fig. 5a, the residual,  $\rho$ , which serves to measure the error induced by the truncation  
 to only the first three modes at each pixel. This measure suggests that CIP clusters  
 may require a finer analysis to be better described. In particular, we select and analyze  
 two points with different residual levels, as shown in Fig. 5a. At point A located in  
 the PDMS matrix (see Fig. 5b), the initial force curve is perfectly reconstructed with  
 an error that is less than 1%. In contrast, at point B located inside a cluster of CIP  
 particles, (Fig. 5c), the truncation error (of the order of  $\simeq 10\%$ ) is mostly concentrated  
 at the maximum pull-out force. One possible explanation is that the error results from  
 the unstable mechanism of ‘snap-off’ between tip and sample. However, the hysteretic

277 mechanism of 'snap-off' is out of the scope of this study, and thus we did not further  
278 attempt to reduce the reconstruction error by introducing additional higher order POD  
279 modes.

## 280 6. Conclusions

281 Accessing complex nano- and microstructural morphologies in heterogeneous media is  
282 both a need and a challenge. The recent PF-QNM AFM mode represents a major step  
283 forward to provide such fine information, whereby each image pixel is fully characterized  
284 by a complete mechanical test. However, the analysis of the resulting large data-sets  
285 becomes not only delicate (because of the intrinsic coupling of different mechanical  
286 and chemical properties with the topography), but also time-wise prohibitive. This  
287 letter has shown that model reduction techniques (such as the POD), can be extremely  
288 useful in organizing hierarchically such large data-sets allowing not only to identify  
289 a small number of modes expressing the underlying phases but also to offer an easy  
290 segmentation of the (mechanically relevant) phases. Starting from the force-indentation  
291 response, proper classification may reveal discrete material responses, allowing to extract  
292 seamlessly the mechanical, chemical or physical response of each of them. In materials  
293 with complex microstructures, the proposed processing may indicate, at first sight,  
294 that mechanical properties are continuously varying making a manual identification  
295 impossible. The POD method allows to properly identify the data points belonging to  
296 the same phase and possibly to a transition region between them.

297 We close by emphasizing that the agnostic character of the data processing  
298 techniques used here is both a strength — no bias is introduced by enforcing say a  
299 contact model that would be unsuited — and a weakness — the physical interpretation  
300 (*e.g.* elastic stiffness, adhesive properties, viscoelasticity) remains in the hand of the  
301 user. However, this interpretation becomes now substantially easier and more robust  
302 since only a reduced subspace of a much lower dimensionality (*i.e.* modes) needs to be  
303 considered.

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310 **Appendix A. PS-LDPE sample**311 *Appendix A.1. Description of the sample*

312 The detailed information concerning the sample type PS-LDPE-12M can be found at the  
 313 following address: <https://www.brukerafmprobes.com/p-3724-ps-ldpe-12m.aspx>

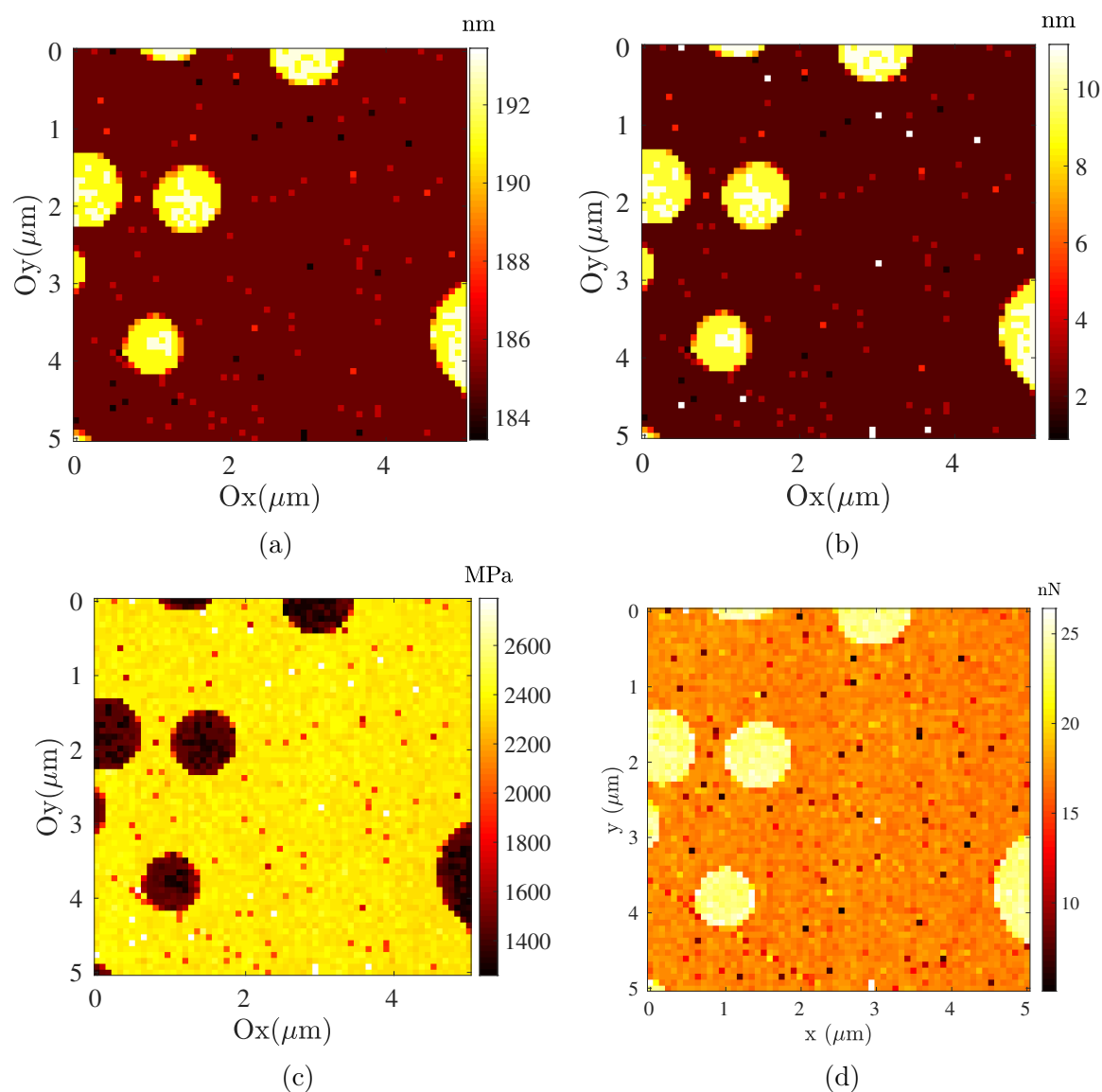
314 *Appendix A.2. QNM properties*

Figure A1: The PF-QNM modality proposed by Bruker provides different mechanical characterizations based on the AFM scan discussed in the main text of the manuscript, relative to the PS-LDPE sample. (a) Topography map; (b) Maximum indentation; (c) Apparent modulus using Hertz model; (d) Adhesion

## 315 Appendix A.3. SEM image

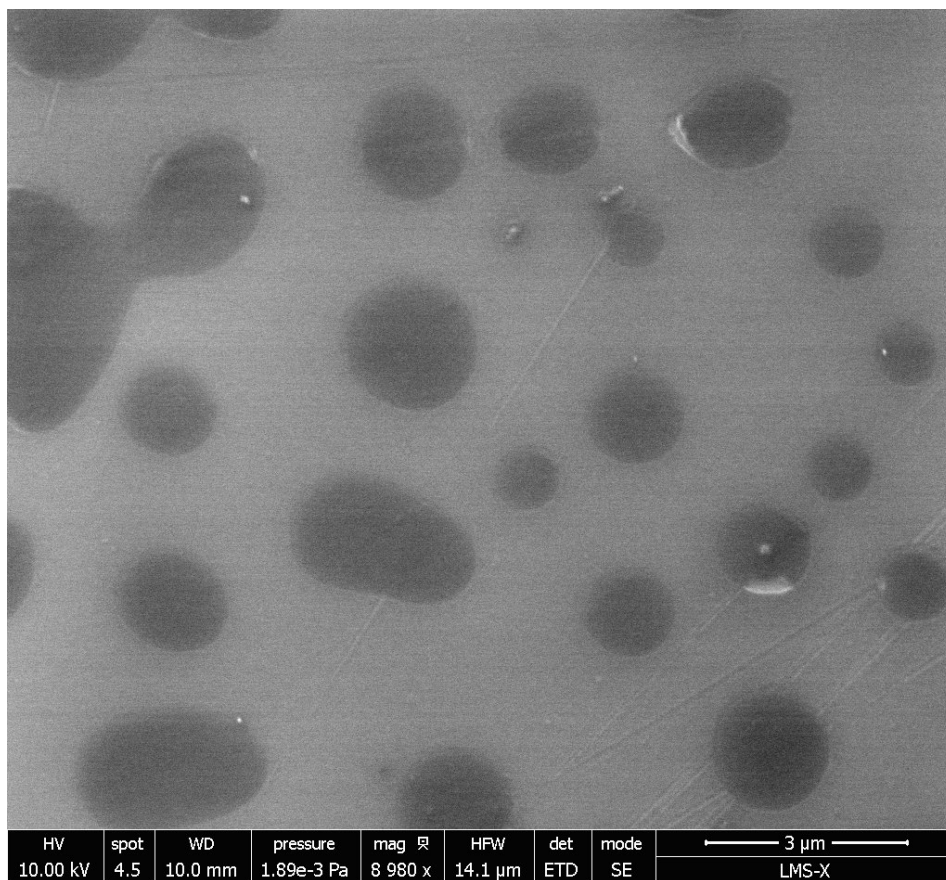


Figure A2: SEM image (secondary electrons) for the PS-LDPE sample (the dark gray domains are the LDPE nanopods while the PS film substrate appears in light gray)



316 **Appendix B. PDMS-CIP sample**317 *Appendix B.1. Fabrication process*

318 The fabrication procedure of the PDMS+CIP composite can be summarized as follows  
319 (see more details in [34]):

- 320 1. The appropriate amount of CIP powder is mixed along with part A + part B (10:1)  
321 of Sylgard 184 in a beaker.
- 322 2. All ingredients are thoroughly mixed for two minutes at 200 RPM mixer.
- 323 3. The mixture is put into a vacuum chamber for 34 minutes to remove the entrapped  
324 air.
- 325 4. The degassed liquid mixture is put in an aluminum mold.
- 326 5. The mold is heated in an oven at temperature  $T = 373$  K for two hours.

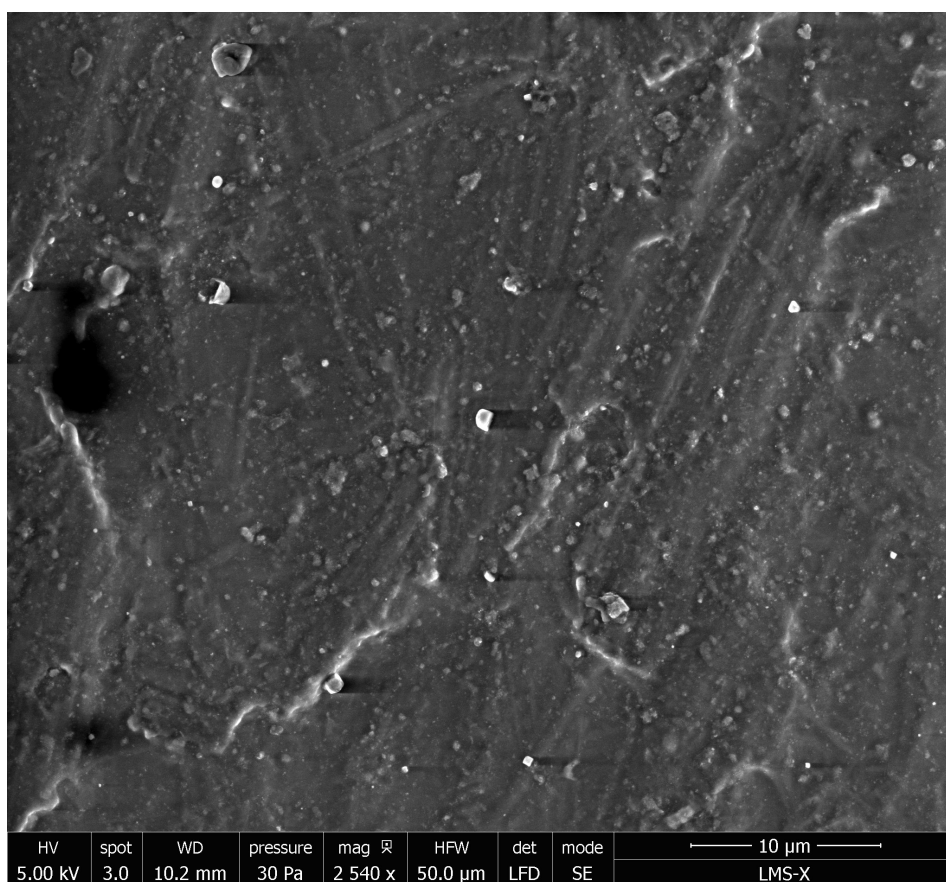
327 *Appendix B.2. SEM image*

Figure B1: SEM image (secondary electrons) for the PDMS-CIP sample. Bright spots originates from the Carbonyl-Iron particles, while the PDMS shows a darker gray level. A significant roughness of the surface is visible

328 **Appendix C. POD truncation**

Note that  $\mathbf{F}$  by construction is not a square (and hence not symmetric). In order to accelerate the computations, we symmetrize  $\mathbf{F}$  in order to form a square matrix of a minimum dimension that allows to obtain seamlessly the eigenvalues  $\lambda^{(n)}$  and the eigenvectors  $\mathbf{W}^{(n)}$ . In the present work, we always have  $N_\delta < N_x$ . As a consequence, the most efficient symmetrization is obtained by setting [30],

$$\mathbf{M} = \mathbf{F}^T \mathbf{F}, \quad \text{or} \quad M_{ij} = \sum_{k=1}^{N_x} F_{kj} F_{ki}. \quad (\text{C.1})$$

This operation leads to a matrix  $\mathbf{M}$  of size  $N_\delta \times N_\delta$ . The alternative one  $\mathbf{F} \cdot \mathbf{F}^T$  would lead to a matrix size of dimension  $N_x \times N_x > N_\delta \times N_\delta$ . Using now the definition introduced in Eq. (2) and simple linear algebra, we can readily get

$$M_{ij} = \sum_{n=1}^{N_\delta} (\lambda^{(n)})^2 W_i^{(n)} W_j^{(n)}. \quad (\text{C.2})$$

329 Thus, use of the symmetric (square) matrix  $\mathbf{M}$  instead of the non-symmetric  $\mathbf{F}$  allows to  
 330 extract in a very simple manner the eigenvalues  $\lambda^{(n)}$  and eigenvectors  $\mathbf{W}^{(n)}$  by employing  
 331 any eigensystem algorithm for symmetric real matrices. Once those two quantities are  
 332 evaluated, one may extract the remaining spatial modes  $\mathbf{U}^{(n)}$  by use of the orthogonality  
 333 between the  $\mathbf{W}^{(n)}$  modes and the direct projection operation, described in Eq. (4).

334 The following algorithm describes the POD operations using this last definition as  
 335 well as the definitions in Section 3.

---

**Algorithm 1: POD truncation**


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**Result:** Compute  $N$  force and spatial modes using POD

Crop Force  $\mathbf{F}$  and indentation  $\boldsymbol{\delta}$  data to selected range;

Resample  $(\mathbf{F}, \boldsymbol{\delta})$  using linear interpolation to a prescribed number of  $\delta$  points;

Force data for all pixels  $i$  and  $\delta_j$  sampling to be gathered into a matrix  $F_{ij}$ ;

Compute the square symmetric matrix  $\mathbf{M} = \mathbf{F}^T \mathbf{F}$ ;

Extract the eigenvalues  $\lambda^{(n)}$  of  $\mathbf{M}$  sorted in decreasing order and the  
 corresponding eigenvectors  $\mathbf{W}^{(n)}$  with  $n = 1, \dots, N_\delta$ ;

Select the appropriate number of modes  $N \ll N_\delta$  from the eigenvalue  
 spectrum;

Compute the corresponding spatial mode  $\mathbf{U}^{(n)} = \frac{1}{\lambda^{(n)}} \mathbf{F} \mathbf{W}^{(n)}$  with  $n = 1, \dots, N$ ;

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