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1 **A general approach based on morphological thermodynamics for a fluid**
2 **confined in various porous media**

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Abstract

37

38 We propose a general approach based on morphological thermodynamics for determining
39 adsorption isotherms, i.e., the chemical potential of a confined fluid as a function of its density. The
40 validity of this approach and its versatility are established by its remarkable accuracy compared to
41 Monte-Carlo simulation results and its capability of accounting for a quite large variety of porous
42 media, ranging from a simple slit pore to a random sponge matrix. It is also revealed that the
43 contribution of the curvature terms to the chemical potential of the confined fluid is negligibly
44 small when the interface curvature is not too large. This finding is of a particular importance for
45 simplifying the treatment of experimental results of adsorption isotherms since no experimental
46 technique is currently available for determining the curvatures of the pore surface inside a porous
47 material.

48

49 **1. Introduction**

50 Porous materials are widely used in various domains, e.g., in chemical industry for molecular sieves
51 and supported catalysts, in new clean energy technology for storing hydrogen, in some new therapy
52 for long-lasting delivery of medicines by encapsulation. It is now well recognized that confinement
53 can modify drastically some properties of adsorbed fluids. Accompanying the advent of many high-
54 performance functionalized nanoporous materials, a large number of experimental and theoretical
55 investigations have been made during the last decades. Nevertheless, a unifying picture
56 highlighting the behavior of confined fluids emerges quite slowly due to the large diversity of
57 structure and morphology for various porous materials. One salient characteristic of fluids confined
58 in porous media is the large interface between fluid and pore wall, which has usually a complex
59 morphology. Although one expects intuitively an important surface contribution to the
60 thermodynamic potentials of such systems, it is not obvious whether it is still possible to define a
61 meaningful surface tension when the characteristic pore size is of the order of a few molecular
62 diameters of the confined fluid. Even if an approach based on thermodynamics is possible, one still
63 needs to know which are the most relevant variables for characterizing the complex interface
64 landscape of fluids adsorbed in porous media. The theoretical study of fluids confined in porous
65 media is still carried out essentially in a case-by-case way. The morphological thermodynamics
66 proposed and advocated by K. Mecke, [R. Roth](#) and co-workers [1-8] provides a framework for a
67 general thermodynamic description of complex interfacial systems. Starting from Hadwiger's
68 theorem in integral geometry, morphological thermodynamics postulates that four geometrical
69 measures are enough to characterize the thermodynamic potential of a complex interfacial system,
70 i.e., volume, surface area, integrated mean curvature and integrated Gauss curvature [1]. Moreover,
71 Mecke et al assume that the thermodynamic variables conjugated to these geometrical measures,
72 i.e. pressure, surface tension, as well as two surface bending rigidities, can be determined for a
73 simple system then be used to describe systems with more complex morphology [1-3]. Although
74 morphological thermodynamics gives promising results for some systems [1-8], the validity of one
75 of its fundamental postulates has been questioned. Theoretical and simulation investigations have
76 provided evidence for the existence of non-Hadwiger terms, i.e., high-order curvature contributions
77 to surface tension, [which are not taken into account in the morphological thermodynamics](#) [9-12].

78 Moreover, these investigations have shown that the first non-Hadwiger term gives a contribution
79 much smaller than the Hadwiger terms, at least one order of magnitude smaller [9]. Hence,
80 morphological thermodynamics can allow for formulating useful approximations in practice even
81 when Hadwiger theorem does not hold rigorously. Fluids adsorbed in porous materials with a
82 complex morphology of pore space provide an interesting ground for further testing the
83 applicability of morphological thermodynamics. This constitutes the main objective of the present
84 work. Some of us (SLZ and WD) have collaborated during a long time with Myroslav Holovko in
85 the study of fluids confined in porous media [13-17]. It is our great pleasure to dedicate the present
86 article to this special issue for the eightieth anniversary of Professor Holovko.

87 Our presentation is organized as follows. A brief introduction of morphological
88 thermodynamics and a general equation of state for a fluid confined in various porous media will
89 be presented in the next section. The accuracy of the general equation of state in different confining
90 media will be assessed in Section III. Some conclusions will be presented in the last section.

91 **2. Theory**

92 ***A. A brief recall of morphological thermodynamics***

93 The morphological thermodynamics proposed by Mecke, Roth and coworkers is based on the
94 fundamental assumption that the grand potential of a complex interfacial system is a linear
95 combination of four morphological measures, i.e., the system's volume, V , the interface area, A ,
96 the integrated mean curvature, C_M , and the integrated Gauss curvatures, C_G . From this assumption,
97 one has immediately the following expression for the grand potential,

$$98 \quad \Omega = -p^{\text{bulk}}(T, \mu)V + \gamma_0(T, \mu)A + \gamma_{-1}(T, \mu)C_M + \gamma_{-2}(T, \mu)C_G, \quad (1)$$

99 where T is temperature, μ the chemical potential. The coefficients of the morphological
100 measures are respectively the pressure of the corresponding bulk system, p^{bulk} , the surface tension
101 on a flat surface, γ_0 , and the bending rigidities, γ_{-1} and γ_{-2} related to the integrated mean and
102 Gauss curvatures. Before applying it to study fluids confined in porous media, it is useful to clarify
103 further some implications of the morphological thermodynamics given in eq.(1). First, it is to note
104 that the morphological measures are completely decoupled with the properties of the fluid, i.e., [the](#)
105 [four morphological measures being independent of the fluid state, i.e., \$T\$ and \$\mu\$.](#) Such decoupling
106 allows for separating the study of a complex interfacial system into two simpler tasks, one for

107 determining the morphological measures in the absence of the fluid and the other for determining
 108 the coefficients, γ_0 , γ_{-1} and γ_{-2} , from a simpler system, e.g., the considered fluid near a
 109 spherical surface. **On the other hand, the independence of the morphological measures on the fluid**
 110 **state does not hold for fluid adsorption in very flexible porous materials since the adsorption can**
 111 **induces large deformation of the materials and modify significantly their morphology. So, the**
 112 **morphological thermodynamics as presented above cannot be applied for the fluid adsorption in**
 113 **flexible porous materials.** We can also rewrite eq.(1) as,

$$114 \quad \Omega = \Omega^{\text{bulk}} + \hat{\gamma}A \quad , \quad (2)$$

115 where

$$116 \quad \hat{\gamma} = \gamma_0(T, \mu) + \gamma_{-1}(T, \mu) \frac{C_M}{A} + \gamma_{-2}(T, \mu) \frac{C_G}{A} \quad . \quad (3)$$

117 Recently, one of us has shown that it is necessary to introduce the concepts of differential and
 118 integral surface tensions for strongly confined fluids, **i.e., pore size being sufficiently small so that**
 119 **γ_0 , γ_{-1} and γ_{-2} in eq.(3) can also depends on the pore size in addition of T and μ [18,19].**
 120 Although $\hat{\gamma}$ defined from eq.(2) is an integral surface tension, the assumption that γ_0 , γ_{-1} and
 121 γ_{-2} are only functions of temperature and chemical potential is too restrictive to account for more
 122 complex situations. Therefore, we can anticipate that the morphological thermodynamics can
 123 become less and less accurate when confinement becomes stronger and stronger.

124 ***B. Adsorption isotherms based on morphological thermodynamics***

125 The morphological thermodynamics extends Gibbs surface thermodynamics by proposing a
 126 concrete recipe to account for the curvature contributions in the grand potential. It is
 127 straightforward to show that the surface tension given in eq.(3) satisfies Gibbs adsorption equation,
 128 i.e.,

$$129 \quad \left(\frac{\partial \hat{\gamma}}{\partial \mu} \right)_{T, C_M, C_G} = \frac{1}{A} \left[\left(\frac{\partial \Omega}{\partial \mu} \right)_{T, C_M, C_G} - \left(\frac{\partial \Omega^{\text{bulk}}}{\partial \mu} \right)_T \right] = - \frac{N_1 - N^b}{A} = -\Gamma \quad , \quad (4)$$

130 where Γ is defined as adsorption, N_1 and N^b are respectively the particle number of the
 131 confined fluid and that of the corresponding bulk fluid in the same volume with the same
 132 temperature and chemical potential. This equation provides a relation between the density of the
 133 confined fluid, $\rho_1 = N_1 V^{-1}$, and that of the corresponding bulk fluid, $\rho^b = N^b V^{-1}$,

$$134 \quad \rho^b = \rho_1 + \left(\frac{\partial \hat{\gamma}}{\partial \mu} \right)_{T, C_M, C_G} \frac{A}{V} \quad . \quad (5)$$

135 Now, from the equation of state of the bulk fluid and the relation given by eq.(5), we obtain
 136 immediately the following equation of state for the confined fluid,

$$137 \quad \mu(\rho_1) = \mu^{\text{bulk}}\left(\rho_1 + \left(\frac{\partial \gamma}{\partial \mu}\right)_{T, C_M, C_G} \frac{A}{V}\right) . \quad (6)$$

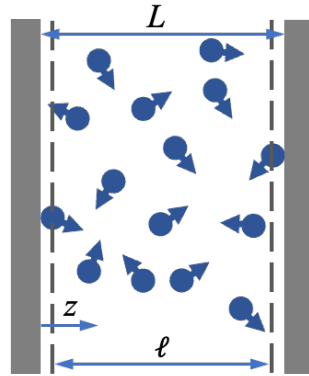
138 3. Results and discussion

139 The theoretical framework presented in the last section is a quite general one which can be applied
 140 for studying a large variety of confined fluids. We illustrate this by considering some benchmark
 141 model systems.

142 A. A hard sphere fluid confined in a slit pore with hard walls

143 We consider first a hard sphere (HS) fluid confined in a slit pore **formed with two parallel hard**
 144 **walls**. A schematic presentation of such a system is given in Figure 1. The morphological
 145 thermodynamic approach described in Section 2.B is based on two prerequisites: i) an equation of
 146 state for the bulk fluid; ii) the surface tension for the considered interface. For a HS fluid confined
 147 in a slit pore with two hard walls, scaled particle theory (SPT) [20-22] provides both the equation
 148 of state of the bulk fluid and the surface tension of a HS fluid near a flat hard wall.

149



150 Figure 1. Schematic presentation of a fluid of hard spheres (blue spheres) confined in a slit pore
 151 with two walls (grey) separated by a distance of L (surface normal along the z -direction). The
 152 dashed lines mark the closest accessible planes for the hard-sphere centers, $l = L - \sigma$ being the
 153 accessible width (σ : fluid hard sphere diameter).

154 The SPT equation of state for a bulk HS fluid is given by,

$$155 \quad \beta\mu^{\text{SPT}} = \ln(\Lambda^3 \rho^b) - \ln(1 - \eta^b) + \frac{7\eta^b}{1 - \eta^b} + \frac{15}{2} \left(\frac{\eta^b}{1 - \eta^b}\right)^2 + 3 \left(\frac{\eta^b}{1 - \eta^b}\right)^3 . \quad (7)$$

156 where Λ is the thermal wavelength, $\beta = (k_B T)^{-1}$ (k_B : Boltzmann constant), $\eta^b = \pi\sigma^3\rho^b\delta^{-1}$
 157 is the packing fraction of the bulk fluid. The surface tension for a fluid-wall interface and the
 158 adsorption depend on the choice of Gibbs dividing surface. For the present work, we choose the
 159 wall surfaces located at $z = \pm L/2$ as the dividing surfaces (see Fig. 1). For this choice, the SPT
 160 gives the following result for the surface tension,

$$161 \quad \pi\sigma^2\beta\gamma_0^{\text{SPT}} = \frac{3\eta^b}{1-\eta^b} + \frac{9}{2}\left(\frac{\eta^b}{1-\eta^b}\right)^2 \quad . \quad (8)$$

162 From the Gibbs adsorption equation, i.e., eq.(4), and the results given in eqs.(7) and (8), we obtain
 163 straightforwardly the adsorption on one pore wall,

$$164 \quad \pi\sigma^2\Gamma_0^{\text{SPT}} = -\pi\sigma^2\left(\frac{\partial\gamma_0^{\text{SPT}}}{\partial\mu^{\text{SPT}}}\right)_T = -\pi\sigma^2\left(\frac{\partial\gamma_0^{\text{SPT}}}{\partial\eta^b}\right)_T\bigg/\left(\frac{\partial\mu^{\text{SPT}}}{\partial\eta^b}\right)_T = -\frac{3\eta^b(1-\eta^b)}{1+2\eta^b} \quad . \quad (9)$$

165 Since the slit pore is composed of two hard walls, we have the following relation between the
 166 packing fraction of the confined fluid, $\eta_1 = \pi\sigma^3\rho_1\delta^{-1}$, and that of the bulk one,

$$167 \quad \eta_1 = \eta^b + \frac{2\pi\sigma^2\Gamma_0^{\text{SPT}}}{6L^*} = \eta^b - \frac{\eta^b(1-\eta^b)}{L^*(1+2\eta^b)} \quad , \quad (10)$$

168 where $L^* = L\sigma^{-1}$ is the pore width measured with the HS diameter. Since eq.(10) is a second
 169 order polynomial, we obtain the following explicit expression of η^b in terms of η_1 ,

$$170 \quad \eta^b = \frac{1-L^*+2L^*\eta_1+\sqrt{(1-L^*+2L^*\eta_1)^2+4L^*(1+2L^*)\eta_1}}{2(1+2L^*)} \quad . \quad (11)$$

171 Now, the adsorption isotherm for a HS fluid confined in a slit pore is given by,

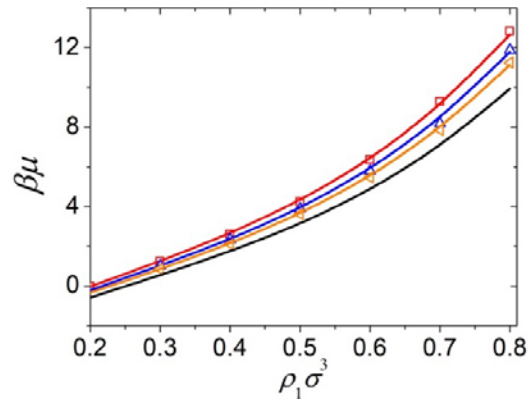
$$172 \quad \beta\mu(\eta_1) = \beta\mu^{\text{bulk}}(\eta^b) \quad . \quad (12)$$

173 The right-hand-side of eq.(12) is given by substituting eq.(11) into eq.(7). Eq. (10) shows clearly
 174 that with the increase of L^* , the difference between η_1 and η^b becomes smaller and smaller and

175 $\lim_{L^*\rightarrow\infty} \eta_1 = \eta^b$, one recovers the bulk result from eq.(12) for $L^* \rightarrow \infty$ as one can expect. For point
 176 particle, i.e. $\sigma = 0$, eqs. (7) and (12) gives the same exact result for the confined and the bulk ideal
 177 gas as we expect.

178 In Figure 2, some results given by eq. (12) are presented for a few pore widths and compared
 179 to the results of Monte-Carlo (MC) simulations. Since the adsorption for this system is negative,
 180 the adsorption isotherms of the confined fluid are always above the isotherm of the bulk fluid. As
 181 the surface contribution decreases when the pore width becomes larger, the isotherm of the confined
 182 fluid approaches more and more the isotherm of the bulk fluid. The agreement between the results

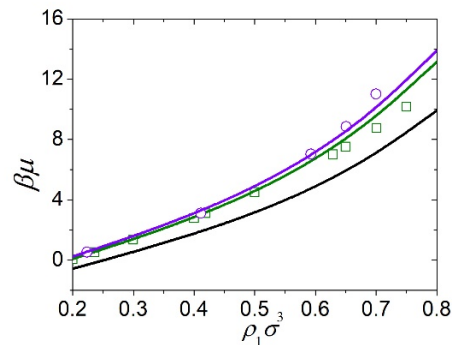
183 of morphological thermodynamics and those of the MC simulations is very good for $L^* \geq 3.5$.



184

185 Figure 2. Chemical potential of a hard sphere fluid confined in a slit pore as a function of fluid
 186 density from morphological thermodynamics, i.e., eq. (12) (continuous line) and *NVT-ensemble*
 187 Monte-Carlo simulations (symbols, see Appendix B for the details about simulation method and
 188 computation conditions). 1) $L^* = 3.5$ (red); 2) $L^* = 5.0$ (blue); 3) $L^* = 7.5$ (yellow); 4) $L^* \rightarrow$
 189 ∞ (black).

190 Figure 3 shows the results for some narrower pores, $L^* \leq 3.0$. Up to the moderate fluid density,
 191 i.e., $\rho_1\sigma^3 \leq 0.6$, morphological thermodynamics gives accurate results. For higher densities, the



192

193 Figure 3. Chemical potential of a hard sphere fluid confined in a narrow slit pore as a function of
 194 fluid density from morphological thermodynamics, i.e., eq. (12) (continuous line) and *NVT-*
 195 *ensemble* Monte-Carlo simulations (symbols, see Appendix B for the details about simulation
 196 method and computation conditions). 1) $L^* = 2.5$ (purple); 2) $L^* = 3.0$ (green); 3) $L^* \rightarrow \infty$
 197 (black).

198 results of morphological thermodynamics deviate more and more from those of the MC simulations.
 199 For very narrow pores, a disjoining pressure [23, 24] arises in the confined fluid. One of us (WD)

200 has shown that due to the contribution of the disjoining pressure, the surface tension for very narrow
201 pores is no longer equal to that for the fluid near one single wall [18]. However, the contribution
202 of the disjoining pressure is not accounted for by the morphological thermodynamics. We believe
203 this is the main reason for the failure of morphological thermodynamics in describing accurately
204 the strongly confined fluids at high densities in very narrow slit pores.

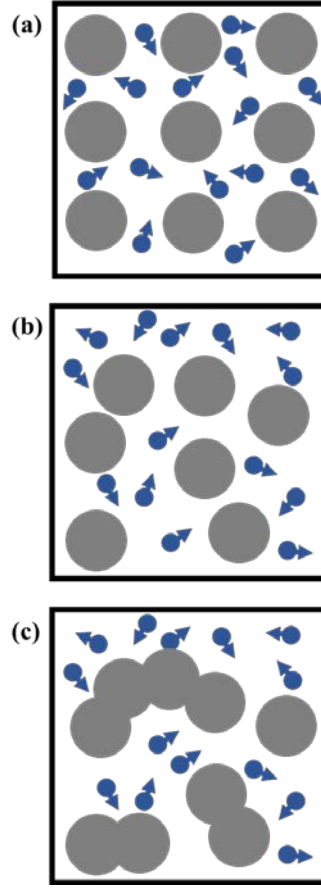
205 **Slit pore** is a model extensively used for studying confined fluids. Many simulations have been
206 carried out for fluids confined in a slit pore. Labik and Smith reported NVT-ensemble Monte Carlo
207 simulation results for hard spheres in a hard slit pore [25] and our simulation results are in good
208 agreement with theirs. Smith and coworkers [26] and Alejandre et al [27] have used integral
209 equations to study a hard sphere fluid in a slit pore. Many investigations on a variety of fluids
210 confined in a slit pore have been made with the help of density functional theory (DFT) and many
211 of them aim at determining the fluid distribution inside the pore (see e.g., [28], an exhaustive review
212 is beyond the scope of the present article). The theoretical approaches based on DFT or integral
213 equations requires first determining the one- and two-body distribution functions. Our approach in
214 this work focuses only on the thermodynamic properties, which requires only the equation of state
215 of the considered fluid in the bulk phase and the surface tension for the considered interface. When
216 SPT is used for these properties, we obtain a totally analytical result for the adsorption isotherms
217 of a hard sphere fluid confined in a slit pore.

218 ***B. A hard sphere fluid confined in an ordered or a disordered hard sphere matrix***

219 The porous matrix model with quenched matrix particles proposed by Madden and Glandt [29]
220 accounts for more characteristics of porous media than the simple slit pore model, e.g., pore
221 connectivity, curved pore surface, variation of pore size inside a porous material. Figure 4 illustrates
222 three types of porous matrices: i) ordered hard sphere matrix with matrix particles fixed on a lattice;
223 ii) disordered hard sphere matrix with matrix particles quenched from an equilibrium configuration
224 of a fluid [29]; iii) overlapping hard sphere matrix with matrix particles distributed totally randomly
225 in space. By construction, the morphological thermodynamics cannot distinguish the matrices of
226 types i and ii. When the dividing surface is chosen as the surface of HS matrix particles, the fluid-
227 matrix interface area of type i or ii matrices can be calculated easily and we have,

$$228 \quad A = \pi\sigma_0^2 N_0 \quad , \quad (13)$$

229 where N_0 and σ_0 are respectively the number and diameter of the matrix particle.



230

231 Figure 4. Schematic presentation of a fluid of hard spheres (blue spheres) confined in different
 232 porous matrices composed quenched matrix particles (grey). a) ordered porous matrix with hard
 233 sphere matrix particles fixed on a simple cubic lattice; b) hard sphere matrix quenched from an
 234 equilibrium liquid configuration; c) overlapping hard sphere matrix with matrix particles
 235 distributed totally randomly in space.

236 The fundamental assumption of the morphological thermodynamics for treating the type i and
 237 type ii matrices is to describe the adsorption as the sum of adsorption around each matrix particle.
 238 SPT gives the following result for the adsorption around the surface of one matrix particle,

$$\begin{aligned}
 239 \quad \pi\sigma_0^2\Gamma_s^{\text{SPT}} &= -\pi\sigma^2 \left(\frac{\partial\gamma^{\text{SPT}}}{\partial\mu^{\text{SPT}}} \right)_{T,\sigma_0} = -\pi\sigma^2 \left(\frac{\partial\gamma^{\text{SPT}}}{\partial\eta^b} \right)_{T,\sigma_0} / \left(\frac{\partial\mu^{\text{SPT}}}{\partial\eta^b} \right)_{T,\sigma_0} \\
 240 \quad &= -\frac{3\eta^b(1-\eta^b)}{1+2\eta^b} \left[\tau^2 + \frac{\tau(1-\eta^b)}{1+2\eta^b} + \frac{(1-\eta^b)^2}{3(1+2\eta^b)} \right] \quad , \quad (14)
 \end{aligned}$$

241 where $\tau = \sigma_0/\sigma$ is the size ratio between the matrix and fluid particles (σ_0 : matrix particle
 242 diameter). Besides the contribution given by eq.(14), there is also an additional contribution to the

243 adsorption given by,

$$244 \quad \pi\sigma_0^2\Gamma_0 = \frac{(\phi_0^{\text{HS}}-1)\rho^b V}{N_0} \quad , \quad (15)$$

245 where V is the volume of the matrix sample and ϕ_0^{HS} the geometric porosity for a hard sphere
246 matrix,

$$247 \quad \phi_0^{\text{HS}} = 1 - \frac{\pi\sigma_0^3 N_0}{6V} = 1 - \eta_0 \tau^3 \quad , \quad (16)$$

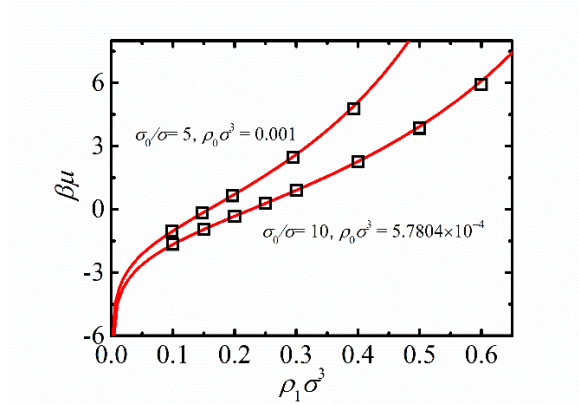
248 with $\eta_0 = \pi\sigma^3 N_0 V^{-1} \tau^3$. Now, the relation between the packing fraction of the confined fluid
249 and that of the bulk fluid with the same chemical potential is given by,

$$250 \quad \eta_1 = \phi_0^{\text{HS}} \eta^b - \frac{3\eta_0 \eta^b (1-\eta^b)}{(1+2\eta^b)} \left[\tau^2 + \frac{\tau(1-\eta^b)}{1+2\eta^b} + \frac{(1-\eta^b)^2}{3(1+2\eta^b)} \right] \quad . \quad (17)$$

251 Unlike the case of a slit pore, it is not possible to solve eq.(17) for obtaining an analytical expression
252 of η^b in terms of η_1 like eq.(11). Nevertheless, it is still quite easy to obtain the adsorption
253 isotherm of the confined fluid with the following procedure. With a given ρ^b , one obtains a value
254 of chemical potential, μ , and the fluid density of the confined fluid having the same chemical
255 potential is given by eq.(17), thus the relation between μ and η_1 is found. When the size of the
256 fluid HS shrinks to zero, i.e., $\sigma = 0$, eq.(17) becomes $\rho_1 = \phi_0^{\text{HS}} \rho^b$ and this allows for obtaining
257 the exact result for an ideal gas confined in a HS matrix, i.e., $\beta\mu = \ln(\Lambda^3 \rho_1 / \phi_0^{\text{HS}})$. So, without
258 the additional contribution to the adsorption given in eq.(15), it is impossible to recover the exact
259 ideal gas results in the limit of point particles. A more detailed discussion about this point is
260 presented in Appendix A.

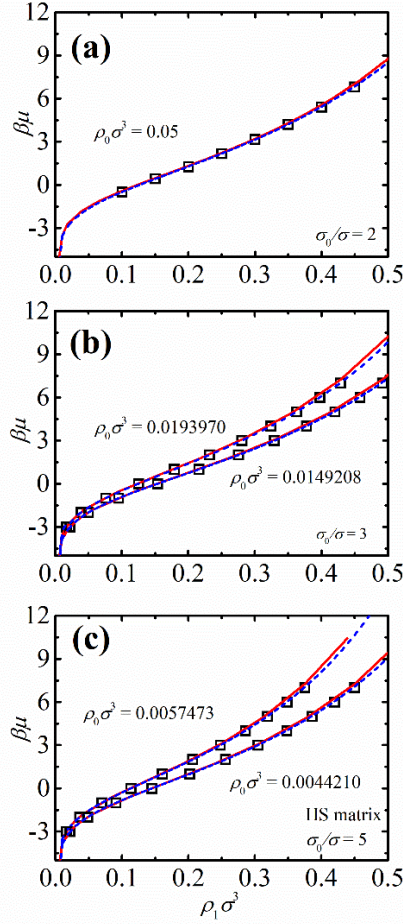
261 The results for a HS fluid confined in two ordered HS matrices with different matrix particle
262 sizes and matrix densities are presented in Fig. 5. The analytical approach by combining
263 morphological thermodynamics and SPT gives excellent results for the chemical potential, as
264 evidenced by the comparison with the results of the Monte-Carlo simulations we performed. **It is**
265 **to note that we define the density of a fluid confined in a porous matrix with respect to the sample**
266 **volume which contains fluid and matrix particles. Due to this definition, the range of fluid densities**
267 **considered for fluids confined in porous matrices appears smaller than that considered for a fluid**
268 **confined in a slit pore. For example, in Figs. 2 and 3 the considered fluid density goes up to 0.8**
269 **while the fluid density considered in Fig. 5 goes only to 0.6. In fact, to make a more plausible**
270 **comparison between the fluid density in a porous matrix and that in a slit pore, we should take into**

271 account the porosity of the porous matrix. For the matrix with $\sigma_0/\sigma = 10$ and $\rho_0\sigma^3 =$
 272 5.7804×10^{-4} in Fig. 5, the porosity is given by $\phi_0 = 1 - \pi\rho_0\sigma_0^3/6 = 0.69734$. Dividing the
 273 fluid density defined with respect to the sample volume by the porosity give the fluid density
 274 defined with respect to the void volume. So, $\rho_1\sigma^3 = 0.6$ corresponds in fact to a fluid density
 275 defined with respect to void volume equal to $\rho_1\sigma^3/\phi_0 = 0.86$.



276
 277 Figure 5. Chemical potential of a hard sphere fluid confined in an ordered porous matrix, with hard
 278 sphere matrix particles fixed on a simple cubic lattice, as a function of fluid density. Matrix to fluid
 279 particle size ratio: $\sigma_0/\sigma = 5, 10$; Matrix density: $\rho_0\sigma^3 = 0.001, 5.7804 \times 10^{-4}$; Red lines:
 280 Morphological thermodynamics combined with SPT; Black squares: *NVT-ensemble* Monte-Carlo
 281 simulation (see Appendix B for the details about simulation method and computation conditions).

282 We consider next the effect of matrix disorder on the chemical potential of the confined fluid.
 283 The results for a HS fluid confined in a disordered HS matrix are presented in Fig. 6. By
 284 construction, the morphological thermodynamics does not take the effect of matrix disorder into
 285 account. However, our Monte-Carlo simulation results given in Fig. 6 are performed for disordered
 286 HS matrices (see Appendix B for simulation methods and computation conditions). The very good
 287 agreement between the results of the morphological thermodynamics and the simulation ones show
 288 that the effect of matrix disorder on the chemical potential is negligibly small. This conforms also
 289 to the same finding of our recent work [30]. In Fig. 6, the results of the morphological
 290 thermodynamics are also compared to those of SPT2b1 theory we proposed previously [16], which
 291 is an approach developed specifically for disordered porous matrices while the morphological
 292 thermodynamics is a general approach applicable for a larger variety of inhomogeneous fluids.



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Figure 6. Chemical potential of a hard sphere fluid confined in a disordered hard sphere matrix as a function of fluid density. a) Matrix to fluid particle size ratio: $\sigma_0/\sigma = 2$; Matrix density: $\rho_0\sigma^3 = 0.05$; b) Matrix to fluid particle size ratio: $\sigma_0/\sigma = 3$; Matrix density: $\rho_0\sigma^3 = 0.0149208, 0.019397$; c) Matrix to fluid particle size ratio: $\sigma_0/\sigma = 5$; Matrix density: $\rho_0\sigma^3 = 0.0044421, 0.0057473$; Red lines: Morphological thermodynamics combined with SPT; Blue dashed lines: SPT2b1 theory [16]; Black squares: Monte-Carlo simulation (Results in (a) from our *NVT*-ensemble Monte-Carlo simulations with the details of simulation method and computation conditions given in Appendix B, those in (b) and (c) from the μVT -ensemble Monte-Carlo simulations given in Table III of [15]).

C. A hard sphere fluid confined in an overlapping hard sphere matrix

The application of morphological thermodynamics to this case follows the general procedure described above. So, we need first determine the porosity of the matrix for a point particle, ϕ_0 , which is required for determining ideal gas contribution to the chemical potential.

$$\begin{aligned}
307 \quad \phi_0^{\text{OHS}} &= \frac{1}{V^{N_0}} \int d\mathbf{r} \prod_{i=1}^{N_0} \int d\mathbf{q}_i e^{-\beta \sum_{j=1}^{N_0} u_{\text{fm}}(|\mathbf{r}-\mathbf{q}_j|)} = \frac{1}{V^{N_0}} \left(V - \frac{4\pi R_0^3}{3} \right)^{N_0} \\
308 \quad &= \exp\left(-\frac{4\pi R_0^3 \rho_0}{3}\right) = \exp(-\eta_0 \tau^3) \quad , \quad (18)
\end{aligned}$$

309 where \mathbf{r} is the position vector of the point particle and \mathbf{q}_i the position vector of the i -th matrix
310 particle. The interaction between the point particle and a matrix particle is given by,

$$311 \quad u_{\text{fm}}(|\mathbf{r}-\mathbf{q}_j|) = \begin{cases} \infty & , & |\mathbf{r}-\mathbf{q}_j| < R_0 \\ 0 & , & |\mathbf{r}-\mathbf{q}_j| \geq R_0 \end{cases} . \quad (19)$$

312 with $R_0 = \sigma_0/2$. The thermodynamic limit is taken, i.e., $\lim_{N_0 \rightarrow \infty, V \rightarrow \infty} N_0/V = \rho_0$, when going to the
313 third equality of eq.(18). The interface area is given by,

$$314 \quad A^{\text{OHS}} = \frac{d(V-\phi_0^{\text{OHS}}V)}{dR_0} = V4\pi R_0^2 \rho_0 \exp\left(-\frac{4\pi R_0^3 \rho_0}{3}\right) = V4\pi R_0^2 \rho_0 \phi_0^{\text{OHS}} \quad . \quad (20)$$

315 The integrated mean and Gauss curvatures are given respectively by,

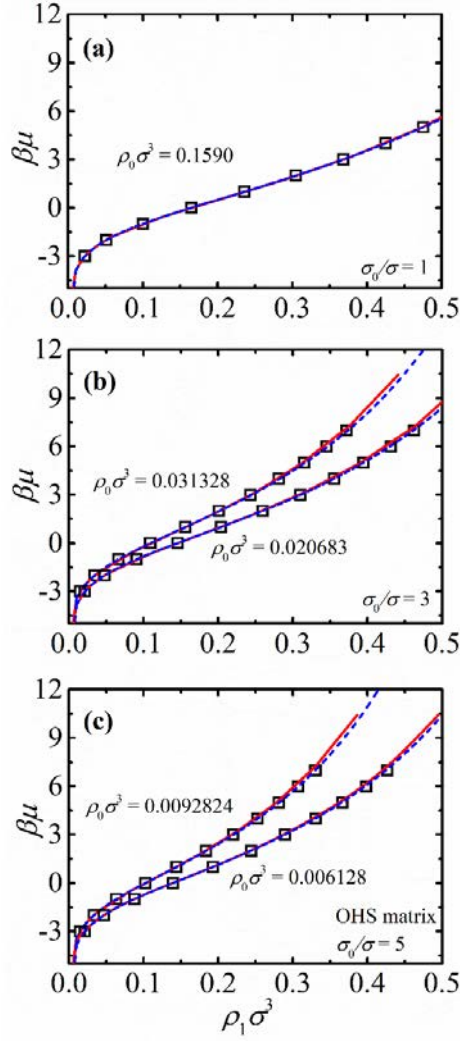
$$\begin{aligned}
316 \quad C_{-1}^{\text{OHS}} &= \frac{1}{2} \frac{dA}{dR_0} = V4\pi R_0 \rho_0 (1 - 2\pi R_0^3 \rho_0) \exp\left(-\frac{4\pi R_0^3 \rho_0}{3}\right) \\
317 \quad &= V4\pi R_0 \rho_0 \left(1 - \frac{3}{2} \eta_0 \tau^3\right) \phi_0^{\text{OHS}} \quad , \quad (21)
\end{aligned}$$

$$\begin{aligned}
318 \quad C_{-2}^{\text{OHS}} &= \frac{1}{2} \frac{d^2 A}{dR_0^2} = V4\pi \rho_0 (1 - 12\pi R_0^3 \rho_0 + 8\pi R_0^6 \rho_0^2) \exp\left(-\frac{4\pi R_0^3 \rho_0}{3}\right) \\
319 \quad &= V4\pi \rho_0 \left(1 - 9\eta_0 \tau^3 + \frac{9}{2} \eta_0^2 \tau^6\right) \phi_0^{\text{OHS}} \quad . \quad (22)
\end{aligned}$$

320 Finally, the morphological thermodynamics combined with SPT gives the following relation
321 between the density of the confined fluid to that of the bulk fluid which has the same chemical
322 potential,

$$\begin{aligned}
323 \quad \eta_1 &= \phi_0^{\text{OHS}} \eta^b - \frac{3\eta_0 \eta^b (1-\eta^b)}{(1+2\eta^b)} \phi_0^{\text{OHS}} \left[\tau^2 + \frac{\tau(1-\eta^b)}{1+2\eta^b} \left(1 - \frac{3}{2} \eta_0 \tau^3\right) \left[+ \frac{(1-\eta^b)^2}{3(1+2\eta^b)} \right] \right. \\
324 \quad &\quad \left. + \frac{(1-\eta^b)^2}{3(1+2\eta^b)} \left(1 - 9\eta_0 \tau^3 + \frac{9}{2} \eta_0^2 \tau^6\right) \right] \quad . \quad (23)
\end{aligned}$$

325 The results for a HS fluid confined in an overlapping hard sphere matrix are presented in Fig.7.
326 The results given by morphological thermodynamics are again in excellent agreement with the
327 simulation ones under all the conditions we have studied.



328

329 Figure 7. Chemical potential of a hard sphere fluid confined in an overlapping hard sphere matrix
 330 as a function of fluid density. Red lines: Morphological thermodynamics combined with SPT; Blue
 331 dashed lines: SPT2b1 theory [16]; Black squares: Monte-Carlo simulation (Results in (a) from our
 332 NVT-ensemble Monte-Carlo simulations with the details of simulation method and computation
 333 conditions given in Appendix B, those in (b) and (c) from μVT -ensemble Monte-Carlo simulations
 334 of [15]). a) Matrix to fluid particle size ratio: $\sigma_0/\sigma = 1$; Matrix density: $\rho_0\sigma^3 = 0.1590$ (the red
 335 line and the blue dashed lines nearly overlap each other); b) Matrix to fluid particle size ratio:
 336 $\sigma_0/\sigma = 3$; Matrix density: $\rho_0\sigma^3 = 0.020683, 0.031328$; c) Matrix to fluid particle size ratio:
 337 $\sigma_0/\sigma = 5$; Matrix density: $\rho_0\sigma^3 = 0.006128, 0.0092824$.

338 **D. A hard sphere fluid confined in a hard sponge matrix**

339 The last system we consider is a hard sphere fluid confined in a hard sponge model proposed by
 340 two of us (SLZ and WD) with Q. H. Liu [31]. Figure 8 gives a schematic presentation of this model.

341 In this case, the interaction potential between a fluid particle and the matrix is a non-additive n-
 342 body one given by,

$$343 \quad v_{\text{fm}}(\mathbf{r}, \mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{N_0}) = -k_B T \ln \left[1 - e^{-\beta \sum_{j=1}^{N_0} u_{\text{fm}}(|\mathbf{r}-\mathbf{q}_j|)} \right] \quad , \quad (24)$$

344 where $u_{\text{fm}}(|\mathbf{r}-\mathbf{q}_j|)$ is given by eq.(19) and now σ_0 is the diameter of a spherical cavity in the
 345 sponge matrix. Although this fluid-matrix interaction potential is non-additive, it is still possible to
 346 obtain an analytical result for the porosity, i.e.,

$$\begin{aligned} 347 \quad \phi_0^{\text{HSG}} &= \frac{1}{V V^{N_0}} \int d\mathbf{r} \prod_{i=1}^{N_0} \int d\mathbf{q}_i e^{-\beta v_{\text{fm}}(\mathbf{r}, \mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{N_0})} \\ 348 \quad &= \frac{1}{V V^{N_0}} \int d\mathbf{r} \prod_{i=1}^{N_0} \int d\mathbf{q}_i \left[1 - e^{-\beta \sum_{j=1}^{N_0} u_{\text{fm}}(|\mathbf{r}-\mathbf{q}_j|)} \right] \\ 349 \quad &= 1 - \frac{1}{V^{N_0}} \left(V - \frac{\pi \sigma_0^3}{6} \right)^{N_0} = 1 - \exp \left(-\frac{\pi \sigma_0^3 \rho_0}{6} \right) = 1 - \phi_0^{\text{OHS}} \quad . \quad (25) \end{aligned}$$

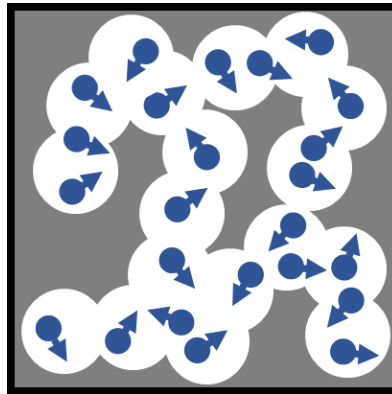
350 The thermodynamic limit is taken, i.e., $\lim_{N_0 \rightarrow \infty, V \rightarrow \infty} N_0/V = \rho_0$, when going to the fourth equality
 351 of eq.(25). It is not difficult to see that if the cavity diameter is the same as that of the matrix particle
 352 in an OHS matrix and their number densities are also equal, the following relations hold between
 353 the interface area, integrated mean and Gauss curvatures of the hard sponge matrix and those of
 354 the OHS matrix,

$$355 \quad A^{\text{HSG}} = A^{\text{OHS}} \quad , \quad (26)$$

$$356 \quad C_{-1}^{\text{HSG}} = -C_{-1}^{\text{OHS}} \quad , \quad (27)$$

$$357 \quad C_{-2}^{\text{HSG}} = C_{-2}^{\text{OHS}} \quad . \quad (28)$$

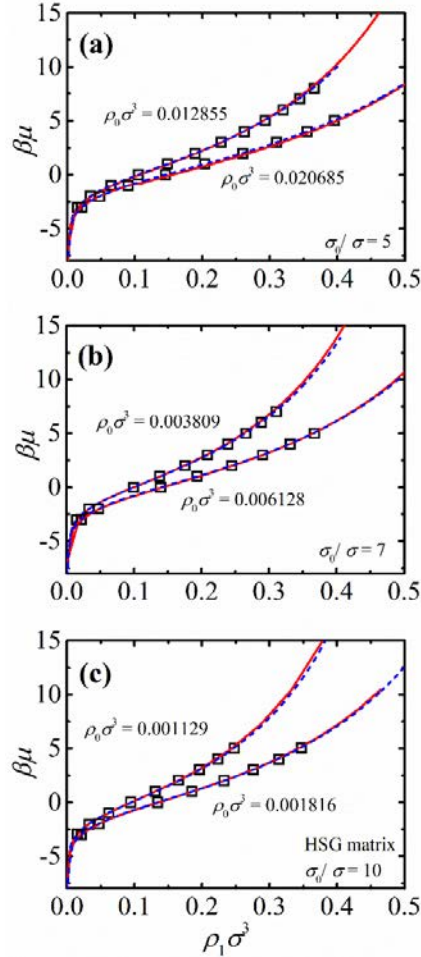
358 The relation given in eq.(27) reflects the simple fact that the confined fluid is adsorbed on a convex
 359 surface in a OHS matrix but on a concave surface in a hard sponge matrix.



360
 361 Figure 8. Schematic presentation of a fluid of hard spheres (blue spheres) confined in a hard sponge

362 matrix (grey).

363 In figure 9, the results of the morphological thermodynamics for a HS fluid in a hard sponge
364 matrix are presented along with simulation results under different conditions. The accuracy of our
365 approach based on the morphological thermodynamics is again remarkable.

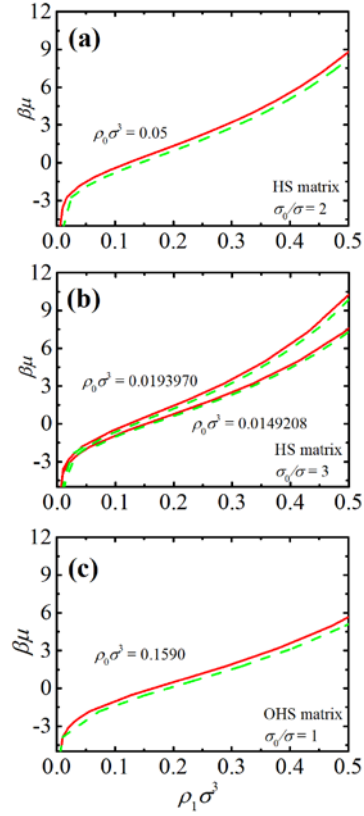


366
367 Figure 9. Chemical potential of a hard sphere fluid confined in a hard sponge matrix as a function
368 of fluid density. a) Cavity to fluid particle size ratio: $\sigma_0/\sigma = 5$; Cavity center density:
369 $\rho_0\sigma^3 = 0.020685, 0.012855$; b) Cavity to fluid particle size ratio: $\sigma_0/\sigma = 7$; Cavity center
370 density: $\rho_0\sigma^3 = 0.006128, 0.003809$; c) Cavity to fluid particle size ratio: $\sigma_0/\sigma = 10$; Cavity
371 center density: $\rho_0\sigma^3 = 0.001816, 0.001129$; Red lines: Morphological thermodynamics
372 combined with SPT; Blue dashed lines: SPT2b1 theory [16]; Black squares: μVT -ensemble Monet-
373 Carlo simulations (results from Fig. 4 of [16]).

374 *D. Contribution of surface curvatures*

375 The comparison of the respective results for OHS and hard sponge matrices indicates that the

376 contribution of the surface curvature terms to the adsorption isotherm can be quite small. More
 377 detailed analyses show that when the matrix particle is three times larger than the fluid particle, the
 378 contribution of the surface curvatures is negligible. Figure 10 shows that even for the size ratio



379
 380 Figure 10. Comparison of the results for the chemical potential of a confined fluid given by the full
 381 morphological thermodynamics (full orange lines) and by its simplified version without the
 382 contribution of curvature terms (dashed green lines). a) a HS fluid in a HS matrix with size ratio
 383 $\sigma_0/\sigma = 2$ and matrix density $\rho_0\sigma^3 = 0.05$; b) a HS fluid in a HS matrix with size ratio
 384 $\sigma_0/\sigma = 3$ and matrix density $\rho_0\sigma^3 = 0.0149208, 0.019397$; c) a HS fluid in an overlapping HS
 385 matrix with size ratio $\sigma_0/\sigma = 1$ and matrix density $\rho_0\sigma^3 = 0.1590$.

386 ($\tau = \sigma_0/\sigma$) equal to 1, 2 or 3, the contribution of the surface curvatures is quite moderate. Bryk et
 387 al have studied the adsorption of hard spheres confined between two uniaxial cylinders by using
 388 DFT. They compared the results for such a confined fluid with those for a HS fluid confined in a
 389 slit pore of two flat walls and found that the surface curvature effect is quite small [32]. Our results
 390 presented in Fig. 10 are consistent with their finding. To the best of our knowledge, there exist no
 391 experimental technique for measuring the interface curvatures of any porous materials. So, our

392 finding here provides a simplified procedure to interpret the experimental results for adsorption
393 isotherms by neglecting the contribution of surface curvature terms.

394 **4. Conclusion**

395 In the present work, we propose a general approach based on the morphological thermodynamics
396 for determining the chemical potential of a fluid confined in a large variety of porous media, from
397 a simple slit pore to a random hard sponge matrix. Our approach requires an equation of state of
398 the considered fluid in a bulk phase and the surface tension of the fluid on a wall with a much
399 simpler morphology than the complex porous medium under consideration. For the hard sphere
400 fluid confined in the various hard porous media considered in this work, scaled particle theory
401 gives both the equation of state of the bulk fluid and the surface tension for a HS fluid on a hard-
402 sphere wall. These are enough for constructing a totally analytical approach for all porous media
403 considered in the present work. The comparison with simulation results show that the overall
404 accuracy of our approach is excellent. Moderate discrepancies are found only for very narrow slit
405 pores ($L \leq 3\sigma$) and at high fluid densities.

406 Although previous investigations have shown that non-Hadwiger terms (high-order curvature
407 terms not included in morphological thermodynamics) do not vanish rigorously [9-12], their
408 contributions are usually smaller by one order of magnitude. In the present work, we find that even
409 the integrated mean and Gauss curvature terms have a negligible contribution to the chemical
410 potential of the confined fluid when the surface curvature is not too large. So, even the contribution
411 of the integrated mean and Gauss curvatures can be neglected in many cases. This simplify
412 significantly the treatment of the experimental results for the adsorption isotherms in practice since
413 the experimental technique is currently lacking for measuring the interface curvatures inside a
414 porous material. Thus, it is in principle possible to elaborate an experimental method for
415 determining the surface tension for the interface between a fluid and the pore wall inside a porous
416 material, with the help of its adsorption isotherms.

Appendix A. An ideal gas confined in a hard sphere matrix

417

418 In this appendix, we show how surface thermodynamics can be applied for an ideal gas adsorbed
 419 in a hard sphere matrix and how the surface tension can be defined in this case. As in the main text,
 420 we consider a grand canonic ensemble. The fluid-matrix interaction is given by,

$$421 \quad \mathcal{V} = \sum_{i=1}^N \sum_{j=1}^{N_0} u_{\text{fm}}(|\mathbf{r}_i - \mathbf{q}_j|) \quad , \quad (\text{A1})$$

422 where \mathbf{r}_i is the position vector of i th fluid particle and \mathbf{q}_j the position vector of j th matrix particle.

423 The interaction potential between a fluid particle and a matrix particle is given by,

$$424 \quad u_{\text{fm}}(|\mathbf{r}_i - \mathbf{q}_j|) = \begin{cases} \infty & , & |\mathbf{r}_i - \mathbf{q}_j| < R_0 \\ 0 & , & |\mathbf{r}_i - \mathbf{q}_j| \geq R_0 \end{cases} . \quad (\text{A2})$$

425 The partition is given by,

$$426 \quad \mathcal{E} = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^3 N!} \int_V \prod_{i=1}^N d\mathbf{r}_i e^{-\beta\mathcal{V}} = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^3 N!} \left(V - \frac{4\pi R_0^3 N_0}{3} \right)^N$$

$$427 \quad = \exp \left[\frac{e^{\beta\mu}}{\Lambda^3} \left(V - \frac{4\pi R_0^3 N_0}{3} \right) \right] . \quad (\text{A3})$$

428 One obtains straightforwardly following result for the grand potential,

$$429 \quad \Omega = -k_B T \ln \mathcal{E} = -k_B T \frac{e^{\beta\mu}}{\Lambda^3} V \phi_0^{\text{HS}} . \quad (\text{A4})$$

430 Eq.(A4) shows that the grand partition function does not depend on the configuration of the porous
 431 matrices. So, the disorder of the matrix configurations does not have any influence on the
 432 thermodynamics of this system. Moreover, the grand potential does not depend on the surface area
 433 of the matrix particle. Thus, the immediate consequence of this is that the differential surface
 434 tension is zero, i.e.,

$$435 \quad \gamma = \left(\frac{\partial \Omega}{\partial A} \right)_{T, V, \mu, \rho_0, R_0} = 0 . \quad (\text{A5})$$

436 At the first glance, this indicates that surface thermodynamics does not apply for such a system.

437 However, it is also straightforward to show that the adsorption in this hard sphere matrix is not zero.

438 The number of the confined fluid inside the matrix is given by,

$$439 \quad N^{\text{cf}} = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T, V, A, \rho_0, R_0} = \frac{e^{\beta\mu}}{\Lambda^3} V \phi_0^{\text{HS}} . \quad (\text{A6})$$

440 However, the number of a bulk ideal gas occupying the same volume and having the same
 441 temperature and the same chemical potential is given by,

442
$$N^{\text{bulk}} = \frac{e^{\beta\mu}}{\Lambda^3} V \quad . \quad (\text{A7})$$

443 Eqs.(A6) and (A7) lead immediately to the following nonzero adsorption,

444
$$\Gamma = \frac{N^{\text{cf}} - N^{\text{bulk}}}{A} = \frac{e^{\beta\mu}}{\Lambda^3} \frac{V}{A} (\phi_0^{\text{HS}} - 1) \quad . \quad (\text{A8})$$

445 The well-known Gibbs adsorption equation implies that a nonzero adsorption should lead to a
 446 nonzero surface tension. So, this result seems to be in contradiction with that of eq.(A5) which
 447 shows the surface tension is zero.

448 Now, we will show that there is in fact no contradiction. It is recently revealed that two surface
 449 tensions can arise, one is the differential surface tension and the other is the integral surface
 450 tension[18, 19]. Moreover, it is the integral surface tension which satisfies a generalized Gibbs
 451 adsorption equation [18]. The integral surface tension includes a contribution from the differential
 452 surface tension and another contribution from the disjoining pressure. We calculate now the
 453 disjoining pressure and show it is indeed nonzero for the system considered here. The pressures of
 454 the confined and bulk fluids are given respectively by,

455
$$p = - \left(\frac{\partial \Omega}{\partial V} \right)_{T, A, \mu, \rho_0, R_0} = k_B T \frac{e^{\beta\mu}}{\Lambda^3} \phi_0^{\text{HS}} \quad , \quad (\text{A9})$$

456
$$p^{\text{bulk}} = - \left(\frac{\partial \Omega^{\text{bulk}}}{\partial V} \right)_{T, \mu} = k_B T \frac{e^{\beta\mu}}{\Lambda^3} \quad . \quad (\text{A10})$$

457 Then, one obtains the following result for the disjoining pressure,

458
$$\Pi = p - p^{\text{bulk}} = k_B T \frac{e^{\beta\mu}}{\Lambda^3} (\phi_0^{\text{HS}} - 1) \quad . \quad (\text{A11})$$

459 Disjoining pressure was discovered by Derjaguin in 1930's for a fluid confined between two
 460 closely approached flat solid surfaces [23, 24]. To the best of our knowledge, nonzero disjoining
 461 pressure has never been found for a fluid confined in a fluid confined in a porous matrix. The
 462 integral surface tension is given by,

463
$$\hat{\gamma} = \gamma - \Pi \frac{V}{A} = -k_B T \frac{e^{\beta\mu}}{\Lambda^3} (\phi_0^{\text{HS}} - 1) \frac{V}{A} \quad . \quad (\text{A12})$$

464 One readily check that this integral surface tension and the adsorption given in eq.(8) satisfies the
 465 following generalized Gibbs adsorption equation [18, 19], i.e.,

466
$$\left(\frac{\partial \hat{\gamma}}{\partial \mu} \right)_{T, \hat{\ell}} = -\Gamma \quad , \quad (\text{A13})$$

467 where $\hat{\ell} = V/A$.

468 Finally, we show that accounting adequately for the integral surface tension and the related

469 adsorption allows for introducing properly the porosity, ϕ_0 , into the adsorption isotherms, i.e., the
 470 chemical potential as a function of the density of the confined fluid. From eq.(A7), one has the
 471 following equation of state for the bulk ideal gas,

$$472 \quad \beta\mu^{\text{bulk}} = \ln(\Lambda^3 \rho^{\text{bulk}}) . \quad (\text{A14})$$

473 From eqs.(A6) – (A8), we obtain,

$$474 \quad \rho^{\text{bulk}} = \rho^{\text{cf}} - \Gamma \frac{A}{V} = \rho^{\text{cf}} - \rho^{\text{cf}} \frac{\phi_0^{\text{HS}} - 1}{\phi_0^{\text{HS}}} = \frac{\rho^{\text{cf}}}{\phi_0^{\text{HS}}} , \quad (\text{A15})$$

475 where $\rho^{\text{bulk}} = N^{\text{bulk}}V^{-1}$, $\rho^{\text{cf}} = N^{\text{cf}}V^{-1}$. Substituting eq.(A15) into eq.(A14), we obtain,

$$476 \quad \beta\mu^{\text{bulk}} = \ln\left(\frac{\Lambda^3 \rho^{\text{cf}}}{\phi_0^{\text{HS}}}\right) = \beta\mu^{\text{cf}} . \quad (\text{A16})$$

477 When going to the last equality of eq.(A16), eq.(A6) is used. This achieves the proof that the matrix
 478 porosity enters into the isotherm of adsorption, i.e., the relation between the chemical potential and
 479 the density of the confined fluid, through the adsorption due to the disjoining pressure.

Appendix B. Simulation method and computational conditions

In the main text, accompanying the presentation of the results given by morphological thermodynamics, Monte-Carlo simulation results are also presented to assess the accuracy of theoretical approach in each case. Except those results with their references being indicated, all the other ones are obtained from our own simulations. In this appendix, we summarize the simulation methods and the computation conditions for each porous medium.

1. Fluid in a slit pore

The Monte-Carlo simulation results presented in Figs. 2 and 3 are obtained by our own simulation in a *NVT*-ensemble. The chemical potential is calculated by using the test particle method based on Widom's potential distribution theorem [33]. The two pore walls are respectively placed at $z = \pm L/2$. The pore wall has a square shape of the size $10\sigma \times 10\sigma$. The periodic boundary condition is used in the two directions parallel to the pore walls. For each simulation run, 2×10^5 Monte-Carlo cycles are first performed to prepare the system to equilibrium, then 10^6 MC cycles are performed to calculate the chemical potential.

2. Fluid in various porous matrices

For the ordered porous matrix (results shown in Fig. 5), we studied only the case with matrix particles placed on a simple cubic lattice. A single matrix particle is placed at the center of the cubic simulation box. The periodic boundary condition is applied in three directions to generate a simple cubic lattice. The simulation box has respectively the size of $20\sigma \times 20\sigma \times 20\sigma$ and $36\sigma \times 36\sigma \times 36\sigma$ for the cases of $\sigma_0 = 5\sigma$ and $\sigma_0 = 10\sigma$.

For the disordered HS matrix (results shown in Fig. 6), a matrix sample is first generated with an *NVT*-ensemble Monte-Carlo simulation for 50 hard spheres of diameter σ_0 in a simulation box of the size $10\sigma \times 10\sigma \times 10\sigma$. Then, fluid particles are introduced into the HS matrix and *NVT*-ensemble Monte-Carlo simulations are performed for the confined fluid. The average over matrix configurations is realized with about 10-20 different matrix samples.

For the overlapping hard sphere matrix (results shown in Fig. 7a), 159 matrix particles with the same diameter as the fluid particle, i.e. $\sigma_0 = \sigma$, are placed totally randomly in the simulation box of the size, $10\sigma \times 10\sigma \times 10\sigma$. The average over matrix configurations is realized with 10

508 different matrix samples.

509 As for the slit pore, each simulation for a given matrix sample includes about 2×10^5 Monte-
510 Carlo cycles for preparing the system to equilibrium and 10^6 production cycles for determining
511 the chemical potential. The simulation code can be found on GitHub
512 (<https://github.com/qiaochongzhi/MC-for-ConfinedFluid>).

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