Intrusion of water in hydrophobic crystalline porous materials

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Crystalline porous media: MOFs



















Intrusion/extrusion in hydrophobic porous materials: a thought experiment

 $\Omega = \Delta V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right)$





A. Tintii







Intrusion/extrusion in hydrophobic porous materials: a thought experiment



$\Omega = \Delta P V_v + \gamma \left(A_{lv} + \cos(\theta) A_{sv} \right)$







A. Tintii

onstant, Ewe also tions in the areas nt to express the $I \not\cong \oint_{\partial \Sigma_{sl}} x_{tl} dl, S$ tripte line along $\delta x_n = \cos\theta \, \delta x_{tl},$

her all the varia-

v dS

 $\delta x_{tl} \ dl = 0, \quad (2)$

Thus, thac Inhe liquid-vapor with prescribed) the constraint $_{sv} - \gamma_{sl})/\gamma_{lv} \equiv$ aplace equation it of metastable ndependent; i e ermined by the elow, important n. The pressure ce $h_{\mu, \nu} = p_{\nu}$ is a μ, ν, λ and T. It is as an additional e liquid volume. ated on solutions $\partial I_{\rm eq}/\partial Z$. Since t by (thermodyarly, the equilib-

lace equation is

one is that of minimal $\Omega_{eq}(Z)$ plotted in Fig. 2 [10]. $\Omega_{eq}(Z)$ is defined on three contiguous intervals: [Z_{min}, Z^{*}] (continuous line), [Z^{*}, Z^{**}] (dashed line), and Z^{**}, Z_{max} (dotted-dashed line) each corresponding to a family of Σ_{lv} interfaces of different shape (see the right panel of Fig. 1). When the groove is almost empty, the contact line is pinned to its sharp edges. Here, Σ_{lv} is the family of arcs having curvature $1/R = -2\cos\beta/l$, as sketched in Fig. 1 with a continuous line. For this particular family, condition (ii) is substituted by Gibbs' criterion [13, / which is the equivalent of Young equation of a sharp edge, 7, prescribing $\theta_Y + \phi - \pi \le \beta \le \theta_Y$, where ϕ is the angle formed by the edge and β is defined as in Fig. 1. Ω_{eq} joins smoothly from the first to the sec**ond** domain at $V_l = Z^*$, where $\beta = \theta_{Y}$ (dashed line in Fig. the proof line Reprinted the metricus advances with constant curvature along the groove, and Ω_{ea} scales linearly with Z.

extrusion pressure and hysteresis



 $+\gamma \left(A_{lv} + \cos(\theta)A_{sv}\right)$

 $\tau = \tau_0 \exp \left[\frac{\Delta \Omega_{\text{ing}}}{M_{\text{NOVEMBER 2012}}} k_B T \right]$

responding to a surface Hysteresis originates from the $(1)_{y}$ (1) to a geometr 0.5 ing one rectangular _____ ve as in Fig. 1, by recover guader pressure you must apply different thermodynamic conditions at changingratheobarrier to become ~1 k_BT given V, T, and system geometry. This is tantamount to 3 0.5 changing $p_1 - p_v$ [1]]. Although for more complicated extrusion barriers geometries numerical schemes need to be developed start-ing from the generat theory, in this 2D geometry it is -0.2 possible 25 to derive an analytical expression for the grave teresis by tuning the tace equations is $\theta_{FIO}f_2$ (color potential as a function of the Mirepuid volume filling the lace equation is The equation is a function of the poppalizer volume of light inside the that at given Z a plethora of een CB and W $Av(p,g^{p,p})/\Delta p$ of the of $A^{p,q}$ and A^{0} . (The consist angle xists, each formed by a collection groove having to be $\theta_{Y} = 110^{\circ}$ and the crect work of the groove $\alpha = 100^{\circ}$ such formed by a collection netrie areashed). The grant potential is shifted so that the West the liquid-vapor interfaces having con-



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Giant Negative Compressibility by Liquid Intrusion into Superhydrophobic Flexible Nanoporous Framework Tortora et al, Nano Letters 21, 2848-2853



ECTRO

Int/ext free energy profile vs pressure











Single water molecules "intrusion"







Percolation

Slow intrusion cannot be due to single water molecules crossing 6MR apertures: barrier very low, very low intrusion pressure and no hysteresis



Turning molecular spring into nano-shock absorber: the effect of macroscopic morphology and crystal size on the dynamic hysteresis of water intrusion-extrusion into-from hydrophobic nanopores, Zajdel et al., ACS Appl. Mater. Interfaces 2022, 14, 26699





Proposed mechanism: capillary condensation





Grand Canonical simulations



Sun et al. "High-rate nanofluidic energy absorption in porous zeolitic frameworks", Nat. Mater. 20, 1015 (2021).





Mismatch with experimental evidence







On the mechanism of water intrusion into flexible ZIF-8: liquid is not vapor, Amayuelas et al, submitted [





Cage-by-cage intrusion mechanism











Origin of the intrusion barrier







E L E C T R O NTRUSION

Why cage-by-cage intrusion





Paulo et al, Comm. Phys. 6, 21 2023



$$t_f = t_f^0 e^{\frac{\Omega_f^{\dagger}}{k_B T}}$$

$$t_e = t_e^0 e^{\frac{\Omega_e^{\dagger}}{k_B T}}$$

Effective surface tension in a (porous) medium









Crystallite size dependency in intrusion





Optimization of the Wetting-Drying Characteristics of Hydrophobic Metal Organic Frameworks via Crystallite Size: The Role of Hydrogen Bonding between Intruded and Bulk Liquid, Johnson et al, submitted





Intruded volume shrinking with decreasing size













Stochastic model of intrusion in crystallites







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"Stiffened" ZIF-8







Knebel et al., "Defibrillation of soft porous metal-organic frameworks with electric fields", Science 358, 347 (2017)





Intrusion in a in-plane rigid slab





Interplay between physics of intrusion and chemistry of imidazolate





Zn-N-C-C dihedral angle



Conclusions



- Kinetics and int/ext pressures in nanometric materials with sub-nanometric apertures violate Young-Laplace, which previously we have shown to work for slightly larger apertures
- The process is not capillary condensation, it still looks like front advancing-like, minimizing the pseudo-liquid/pseudovapor interface area
- This mechanism determines the crystallite size dependence of the int/ext pressure
- Stiffened material shows that there is an unknown connection between the physics of intrusion and the chemistry of imidazolate linker





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