

Supporting Information for

Adsorption Thicknesses of Confined Pure and Mixing Fluids in Nanopores

by

Kaiqiang Zhang¹, Na Jia^{1*}, and Lirong Liu²

¹Petroleum Systems Engineering

Faculty of Engineering and Applied Science

University of Regina

Regina, Saskatchewan S4S 0A2

Canada

²Institute for Energy, Environment and Sustainable Communities

University of Regina

Regina, Saskatchewan S4S 0A2

Canada

Figures	5
Equations	25
Pages	13

In the Supporting Information, the detailed derivations for the generalized equation of state (EOS), which considers the effects of pore radius, shifts of critical properties, molecule–molecule and molecule–wall interactions, are specified. Furthermore, the calculated adsorption thicknesses of the C₂H₆, C₃H₈, C₅H₁₂, C₆H₁₄, C₇H₁₆, and C₈H₁₈ substances at different temperatures, pressures, pore radii, and wall-effect distances are shown in Figs. S2–S5.

Derivations of the generalized EOS

In this study, a generalized EOS for the confined fluid in nanopores is obtained, which considers the confinement-induced effects of pore radius, molecule–molecule and molecule–wall interactions.

The canonical partition function from the statistical thermodynamics is shown as follows,¹

$$Q(N, V, T) = \sum_i e^{-E_i(N, V)/kT} = \frac{1}{N!} \Lambda^{-3N} q_{\text{int}}^N Z(N, V, T) \quad (\text{Eq. S1})$$

where N is the number of molecules; V is the volume; T is the temperature; E is the overall energy state; k is the Boltzmann constant; Λ is the de Broglie wavelength, $\Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{0.5}$, h is the Planck's constant, m is the molecular mass; q_{int} is the internal partition function; Z is the configuration partition function, which is expressed as,

$$Z(N, V, T) = \iint_V e^{-U(r_1, r_2, \dots, r_N)/kT} dr_1 dr_2 \dots dr_N \quad (\text{Eq. S2})$$

where U is the potential energy of entire system of N molecules, whose positions are described by r_i , $i = 1, 2, \dots, N$, and r_i is the distance of separation between molecules.

Since the configurational energy (E^{conf}) is expressed as,

$$E^{\text{conf}}(N, V, T) = E(N, V, T) - E(N, V, T = \infty) = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{N, V} \quad (\text{Eq. S3})$$

So,

$$\ln Z(N, V, T) - \ln Z(N, V, T = \infty) = \int_{\infty}^T \frac{E^{conf}(N, V, T)}{kT^2} dT \quad (\text{Eq. S4})$$

where only the hard-core repulsive forces between molecules $Z^{HC}(\rho)$ are important when the configuration integral at infinite temperature, $Z(N, V, T = \infty) = Z^{HC}(\rho)$. $Z^{HC}(N, V, T = \infty) = V_f^N$ is defined from the literature,² where V_f^N is the free volume. Thus, Eq. (S4) can be rewritten as,

$$Z(N, V, T) = V_f^N e^{\left(\int_{\infty}^T \frac{E^{conf}(N, V, T)}{kT^2} dT\right)} \quad (\text{Eq. S5})$$

The free volume V_f^N can be expressed by using the following simple expression,²

$$V_f = V - N\beta = V - \frac{N}{\rho_{\max}} \quad (\text{Eq. S6})$$

where β is the excluded volume per fluid molecule and ρ_{\max} is the molecular density of the full-distributed fluid. Eqs. (S5) and (S6) are substituted into Eq. (S1) to be,

$$Q(N, V, T) = \sum_i e^{-E_i(N, V)/kT} = \frac{1}{N!} \Lambda^{-3N} q_{\text{int}}^N (V - N\beta)^N e^{\left(\int_{\infty}^T \frac{E^{conf}(N, V, T)}{kT^2} dT\right)} \quad (\text{Eq. S7})$$

It is worthwhile to mention that ρ_{\max} is function of the ratio of the pore size (r_p) and fluid molecule size (σ), r_p / σ , whose specific formulation is shown below,³

$$\rho_{\max} = \frac{6}{\pi\sigma^3} (1 - \phi) \quad (\text{Eq. S8})$$

$$\phi = c_1 + c_2 e^{c_3(0.5 - r_p / \sigma)} - c_4 e^{c_5(0.5 - r_p / \sigma)} \quad (\text{Eq. S9})$$

where ϕ is the mean porosity of the porous medium initiated by Mueller (2005)⁴ and $c_i, i=1, 2, 3, 4, 5$ are the numerical coefficients obtained from the curve fitting.³ Eq. (S8) change

to be $\rho_{\max} = \frac{6}{\pi\sigma^3} (1 - c_1)$ when r_p / σ tends to be infinite (i.e., bulk phase), so,

$$\sigma = \sqrt[3]{\frac{6(1-c_1)}{\pi\rho_{\max}}} = \sqrt[3]{\frac{6\beta(1-c_1)}{\pi}} = \sqrt[3]{\frac{6(1-c_1)b}{\pi N_A}} \quad (\text{Eq. S10})$$

where b is the volume parameter of the cubic EOS and N_A is the Avogadro constant.

From the statistical thermodynamics,¹

$$P(N, V, T) = kT \left(\frac{\partial \ln Z(N, V, T)}{\partial V} \right)_{N, T} \quad (\text{Eq. S11})$$

Given that $\frac{1}{N!} \Lambda^{-3N} q_{\text{int}}^N = \text{constant}$, Eq. (S7) is substituted into Eq. (S11) to be,

$$\begin{aligned} P(N, V, T) &= kT \left(\frac{\partial \ln[(V - N\beta)^N e^{\left(\int_{\infty}^T \frac{E^{\text{conf}}(N, V, T)}{kT^2} dT\right)}]}{\partial V} \right)_{N, T} \\ &= \frac{NkT}{V - N\beta} - \frac{\partial \ln(e^{E^{\text{conf}}(N, V, T)}}{\partial V} \end{aligned} \quad (\text{Eq. S12})$$

It is easily found from Eq. (S12) that $E^{\text{conf}}(N, V, T)$ is the key part to explicitly illustrate the relationships of P , V , and T . The configurational energy (E^{conf}) is consist of the configurational energy between molecule and molecule ($E_{\text{molecule-molecule}}^{\text{conf}}$) as well as between the molecule and wall ($E_{\text{molecule-wall}}^{\text{conf}}$), which is demonstrated in Fig. S1 and presented as follows,

$$E^{\text{conf}}(N, V, T) = E_{\text{molecule-molecule}}^{\text{conf}} + E_{\text{molecule-wall}}^{\text{conf}} \quad (\text{Eq. S13})$$

In this study, the molecule–molecule interactions ($E_{\text{molecule-molecule}}^{\text{conf}}$) are expressed as,⁵

$$E_{\text{molecule-molecule}}^{\text{conf}} = \frac{kTN^2}{2V^2} \iint \frac{U_{\text{mm}}(r_1, r_2 \dots r_N)}{kT} g(r; \rho, T) dV_1 dV_2 \quad (\text{Eq. S14})$$

where $g(r; \rho, T)$ is the pair correlation function for molecules interacting through the potential $U(r)$. In the literature, the pair correlation function at low densities was stated clearly,⁶

$$\lim_{\rho \rightarrow 0} g(r; \rho, T) = e^{-u(r)/kT} \quad (\text{Eq. S15})$$

Here, $C = C(N, V, T) = \int_r g(r; \rho, T) dr$. Molecule–molecule interactions $U_{\text{mm}}(r)$ are assumed to be numerically represented through the Lennard-Jones potential, whose schematic diagram is shown in Fig. S1 and numerical equation is,

$$U_{\text{mm}}(r_{12}) = 4\varepsilon_{\text{LJ}} \left[\left(\frac{\sigma_{\text{LJ}}}{r_{12}} \right)^{12} - \left(\frac{\sigma_{\text{LJ}}}{r_{12}} \right)^6 \right] \quad (\text{Eq. S16})$$

where ε_{LJ} is the molecule–molecule Lennard–Jones energy parameter and σ_{LJ} is the molecule–molecule Lennard–Jones size parameter.

Thus, Eq. (S14) is re-written as,

$$E_{\text{molecule-molecule}}^{\text{conf}} = \frac{kTN^2C}{2V^2} \iint_{r_i > \sigma} \frac{U(r_1, r_2 \dots r_N)}{kT} dV_1 dV_2 \quad (\text{Eq. S17})$$

Then, the integral part of Eq. (S17) is solved semi-analytically as,

$$\frac{1}{V} \iint_{r_{12} > \sigma} \frac{U_{\text{mm}}(r_1, r_2 \dots r_N)}{kT} dV_1 dV_2 = \frac{4\varepsilon_{\text{LJ}}}{kT} \sigma_{\text{LJ}}^3 f(A) \quad (\text{Eq. S18})$$

$$f(A) = c_0 + \frac{c_1}{\sqrt{A}} + \frac{c_2}{A}$$

where $c_0 = -\frac{8\pi}{9}$, $c_1 = 3.5622$, and $c_2 = -0.6649$. It should be noted that the value of c_0 was calculated by solving Eq. (S5) analytically, while the values of c_1 and c_2 are obtained from a non-linear least-square method. The calculated $f(A)$ values from Eq. (S5) and fitting curve by tuning c_1 and c_2 can be found elsewhere.⁵ Thus, the molecule–molecule interactions ($E_{\text{molecule-molecule}}^{\text{conf}}$) are presented as,

$$E_{\text{molecule-molecule}}^{\text{conf}} = \frac{aN^2 - 2N^2C\varepsilon_{\text{LJ}}\sigma_{\text{LJ}}^3 \cdot \left(\frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right)}{V} \quad (\text{Eq. S19})$$

On the other hand, the molecule–wall interactions $U_{mw}(r)$ are assumed to be well modeled through the square-well potential, which is shown in Fig. S1 and stated as follows,

$$U_{mw}(r_{ij}) = \begin{cases} +\infty, & r_{ij} < \sigma_{sw-ij} \\ -\varepsilon_{sw-ij}, & \sigma_{sw-ij} \leq r_{ij} \leq (\sigma_{sw-ij} + \delta_{sw-ij}) \\ 0, & r_{ij} > (\sigma_{sw-ij} + \delta_{sw-ij}) \end{cases} \quad (\text{Eq. S20})$$

where r_{ij} is the distance between the molecule and wall; ε_{sw-ij} is the molecule–wall square-well energy parameter; σ_{sw-ij} is the molecule–wall square-well size parameter; and δ_{sw-ij} is the molecule–wall square-well width of interactions, which is assumed to be equal to σ_{LJ} for each system. Hence, the molecule–wall interactions ($E_{molecule-wall}^{conf}$) are expressed as,³

$$E_{molecule-wall}^{conf} = -N \cdot F_p \cdot \varepsilon_{sw} \quad (\text{Eq. S21})$$

where F_p is the fraction of the confined fluid molecules that interact with the pore wall (i.e., in the square-well region). The local distributions of fluid molecules interacting with the pore wall are numerically represented by F_p , which is function of the temperature, fluid density, degree of confinement, and molecule–wall interaction potential.³ An empirical correlation rather than a complex theoretical model is capable of describing F_p in an accurate and simple way as follows,

$$F_p = F_{pr} + (1 - F_{pr})(1 - e^{-\varepsilon_{sw}/kT})(1 - \frac{\rho}{\rho_{max}})^{\theta} \quad (\text{Eq. S22})$$

$$F_{pr} = \frac{(r_p - \sigma/2)^2 - (r_p - \sigma/2 - \delta_p)^2}{(r_p - \sigma/2)^2}$$

$$\theta = \frac{r_p}{\delta_p + \sigma/2}$$

where F_{pr} is the fraction of the random distributed fluid molecules in the square-well region of

the pores and θ is the geometric term. Thus, Eq. (S22) is substituted into Eq. (S21) to be,

$$E_{molecule-wall}^{conf} = -N \cdot \varepsilon_{sw} [F_{pr} + (1 - F_{pr})(1 - e^{-\varepsilon_{sw}/kT})(1 - \frac{\rho}{\rho_{max}})^\theta] \quad (\text{Eq. S23})$$

Hence, the total configurational energy between molecule and molecule as well as between the molecule and wall is obtained by combining Eqs. (S13), (S19), and (S23),

$$E^{conf}(N, V, T) = \frac{aN^2 - 2N^2 C \varepsilon_{LJ} \sigma_{LJ}^3 (\frac{c_1}{\sqrt{A}} + \frac{c_2}{A})}{V} - N \cdot \varepsilon_{sw} [F_{pr} + (1 - F_{pr})(1 - e^{-\varepsilon_{sw}/kT})(1 - \frac{\rho}{\rho_{max}})^\theta] \quad (\text{Eq. S24})$$

On a basis of Eq. (S12), the generalized expression of the EOS for confined fluids considering the effects of pore radius, molecule–molecule, and molecule–wall interactions is shown as,

$$P(N, V, T) = \frac{RT}{V - Nb} - \frac{N^2}{V^2} [a - 2\varepsilon_{LJ} \sigma_{LJ}^3 \cdot (\frac{c_1}{\sqrt{A}} + \frac{c_2}{A})] - \frac{b\theta}{V^2} (1 - \frac{b}{V})^{\theta-1} (1 - F_{pr}) [RT(1 - e^{-N_A \varepsilon_{sw}/RT}) - N_A \varepsilon_{sw}] \quad (\text{Eq. S25})$$

$$b = \frac{N_A}{\rho_{max}}$$

Eq. (S25) is the newly-derived generalized EOS for calculating the fluid phase properties at the nanoscale.

References

- (1) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21* (1), 116–128.
- (2) Sandler, S. I. The Generalized van Der Waals Partition Function. I. Basic Theory. *Fluid Phase Equilib.* **1985**, *19* (3), 238–257.
- (3) Travalloni, L.; Castier, M.; Tavares, F. W.; Sandler, S. I. Thermodynamic Modeling of Confined Fluids Using an Extension of the Generalized van Der Waals Theory. *Chem. Eng. Sci.* **2010**, *65* (10), 3088–3099.
- (4) Mueller, G. E. Numerically Packing Spheres in Cylinders. *Powder Technol.* **2005**, *159* (2), 105–110.
- (5) Zarragoicoechea, G. J.; Kuz, V. A. Van Der Waals Equation of State for a Fluid in a Nanopore. *Phys. Rev. E* **2002**, *65* (2), 21110.
- (6) Islam, A. W.; Patzek, T. W.; Sun, A. Y. Thermodynamics Phase Changes of Nanopore Fluids. *J. Nat. Gas Sci. Eng.* **2015**, *25*, 134–139.

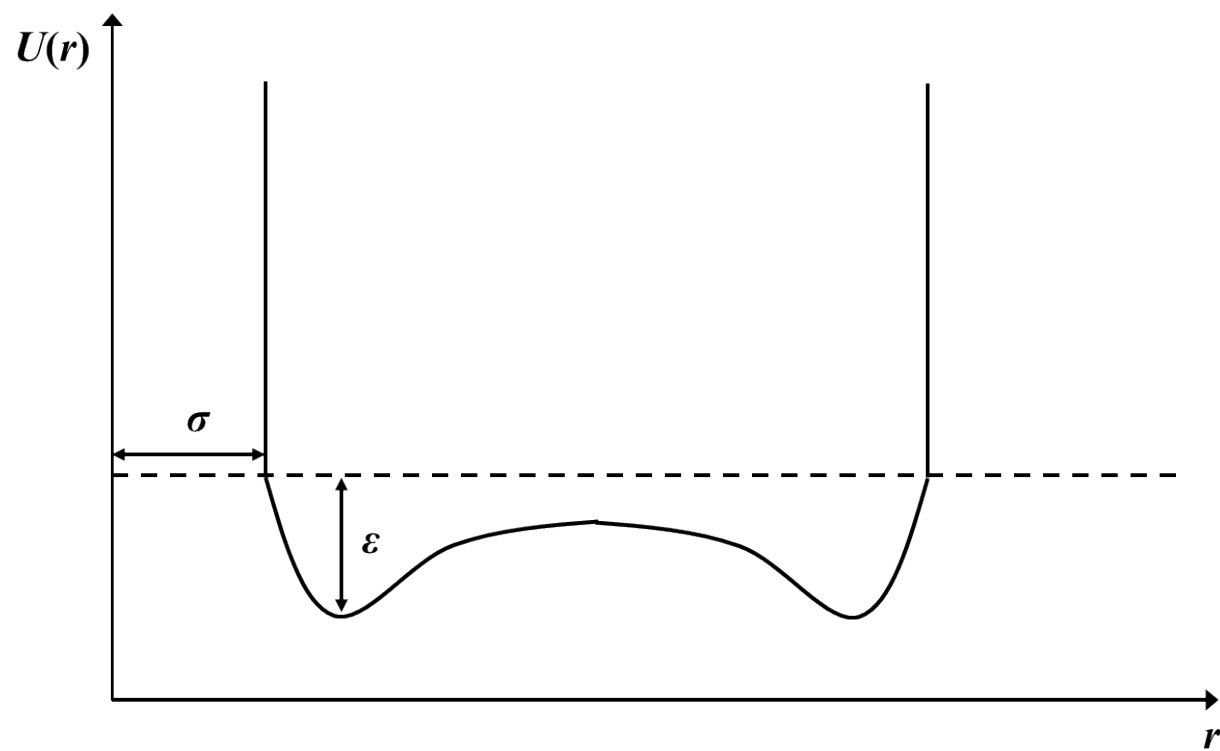


Figure S1. Schematic diagram of the molecule–molecule and molecule–wall potentials in this study.

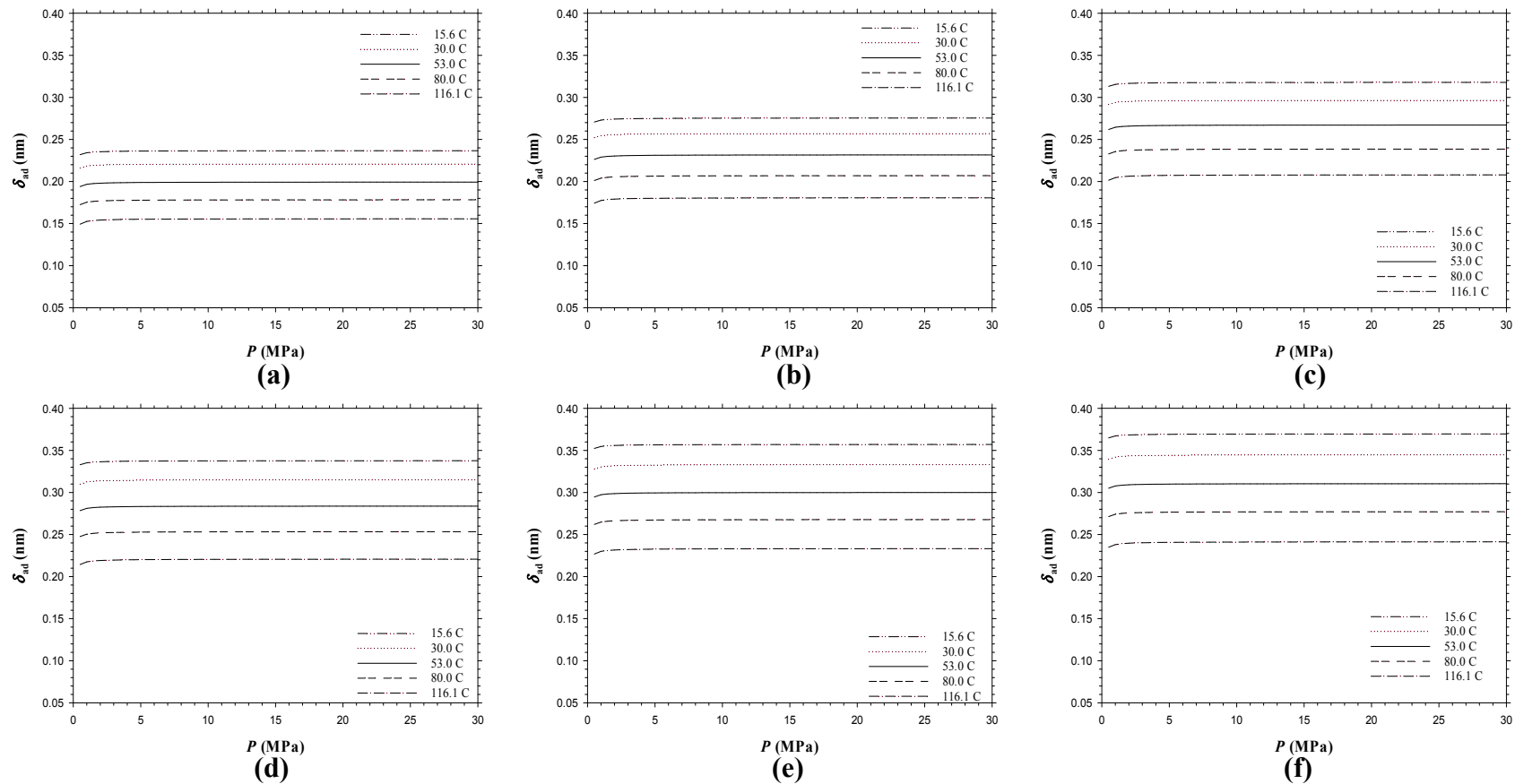


Figure S2. Calculated adsorption thicknesses of the (a) C_2H_6 ; (b) C_3H_8 ; (c) C_5H_{12} ; (d) C_6H_{14} ; (e) C_7H_{16} ; and (f) C_8H_{18} at the pore radius of $r_p = 10$ nm and five different temperatures of $T = 15.6, 30.0, 53.0, 80.0, 116.1$ °C.

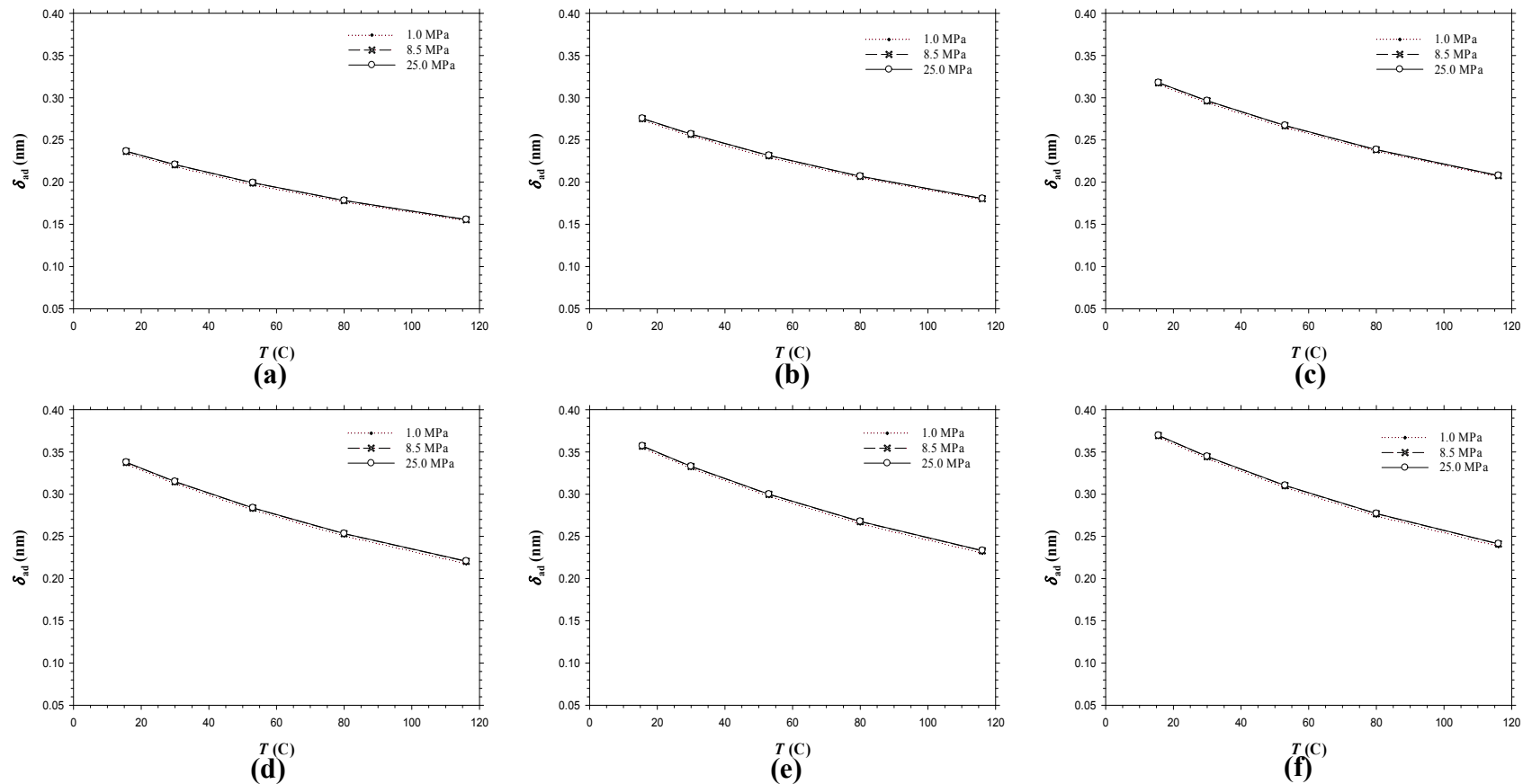


Figure S3. Calculated adsorption thicknesses of the (a) C_2H_6 ; (b) C_3H_8 ; (c) C_5H_{12} ; (d) C_6H_{14} ; (e) C_7H_{16} ; and (f) C_8H_{18} at the pore radius of $r_p = 10$ nm, three different pressures of $P = 1.0, 8.5,$ and 25.0 MPa, and five different temperatures of $T = 15.6, 30.0, 53.0, 80.0,$ and 116.1 °C.

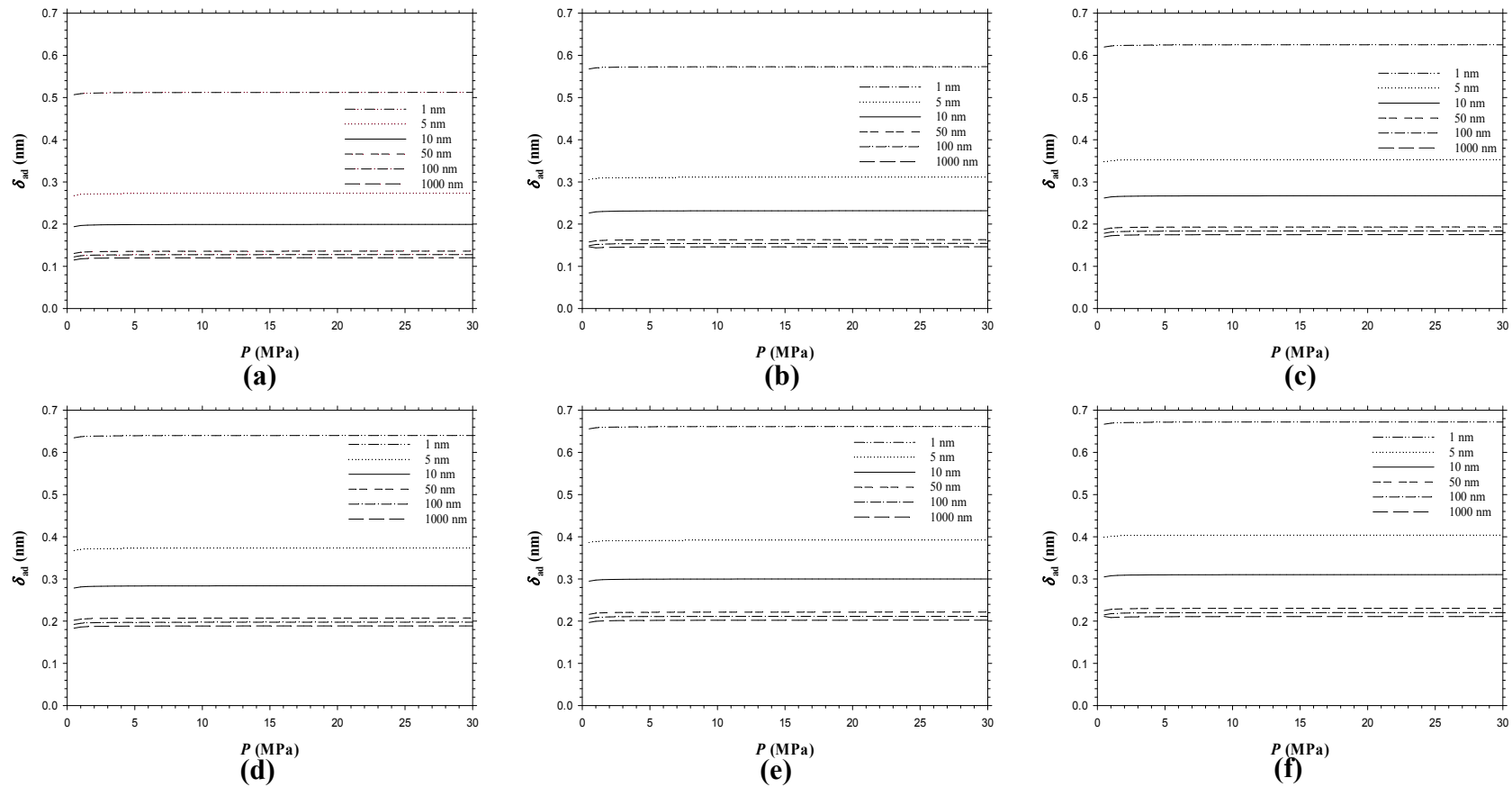


Figure S4. Calculated adsorption thicknesses of the (a) C_2H_6 ; (b) C_3H_8 ; (c) C_5H_{12} ; (d) C_6H_{14} ; (e) C_7H_{16} ; and (f) C_8H_{18} at the temperature of $T = 53.0$ °C and six different pore radii of $r_p = 1, 5, 10, 50, 100$, and 1000 nm.

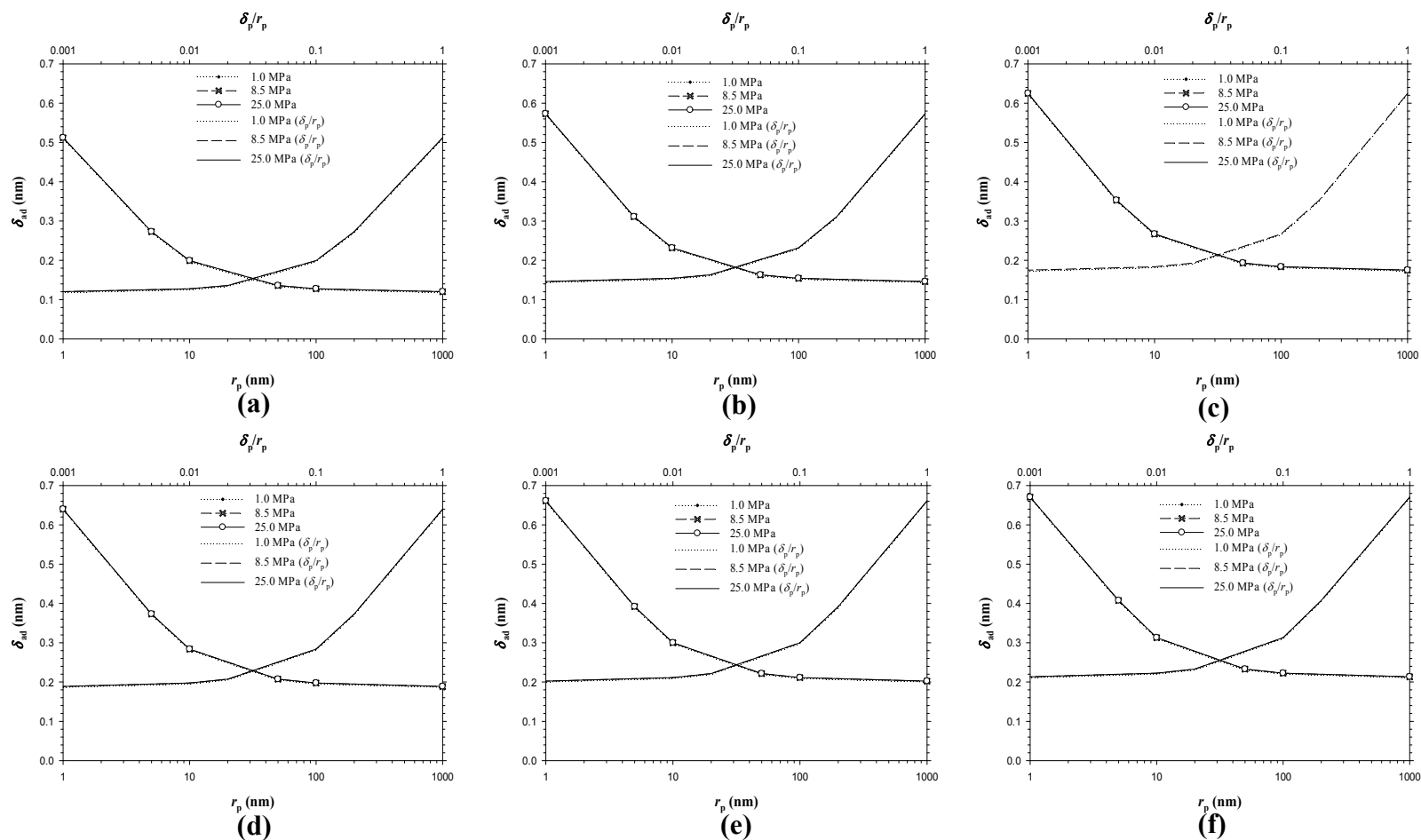


Figure S5. Calculated adsorption thicknesses of the (a) C_2H_6 ; (b) C_3H_8 ; (c) C_5H_{12} ; (d) C_6H_{14} ; (e) C_7H_{16} ; and (f) C_8H_{18} at the temperature of $T = 53.0$ °C, three different pressures of $P = 1.0, 8.5$, and 25.0 MPa, and six different pore radii of $r_p = 1, 5, 10, 50, 100$, and 1000 nm (i.e., $\delta_p/r_p = 1, 0.2, 0.1, 0.02, 0.01$, and 0.001 , respectively).