

An Equation of State for Pore-Confined Fluids

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Introduction

The prediction of properties in porous materials is of continuing interest in the fields of chemical and materials engineering. Application areas include, among others: (1) the use of supercritical fluids to modify porous materials,^{1–4} (2) physical adsorption of trace components from gaseous effluents,⁵ (3) gas storage using microporous materials,⁶ and (4) chemical separations using inorganic membranes.⁷ The confinement of a fluid in a porous matrix changes its properties relative to its bulk state and this may be important in engineering applications. As such, a number of researchers have worked in this area while attempting to advance knowledge in the field. For instance, the interplay between fluid-wall and fluid-fluid interactions, and the effects of confinement and pore geometry in mesoscopic porous materials has been studied theoretically and using computer simulation by Findenegg and collaborators.^{8–10} The effect of confinement on the criticality of fluids in controlled-pore materials with narrow-size distribution has also been studied, indicating a shift of the gas-liquid critical point of the fluid in the porous material to lower temperature. However, the situation is different in amorphous mesoporous materials such as silica aerogel; due to the wide pore-size distribution and ill-defined pore geometry, it has not been possible to establish a quantitative description of the critical point shift.^{11–12} Given this situation, there has been substantial effort over the years devoted to developing equations of state suitable for thermodynamic property predictions in fluids confined in porous media, nevertheless, tractable, physically based models have remained elusive.¹³

An important class of these equations of state are of the mean field type, which are of interest because they are often analytic, and, therefore, amenable for use in process engineering calculations.¹⁴ Two important questions arise in the context of such equations of state: how accurate are they for real fluids and can the required number of adjustable parameters for their use be kept to a minimum and have some physical meaning? Our purpose in this article is to investigate both of these points with respect to the model and approach described here.

For pure fluids, the proposed equation of state only requires the pure fluid critical properties. As a result, we believe that a fair comparison can be made between the proposed model and other equations of state that require similar knowledge, such as the Peng-Robinson (PR) equation of state, one of the most successful engineering cubic equations of state.¹⁵ Our model, however, has an important advantage over the PR equation of state, in that it can be theoretically and rationally extended for calculating thermodynamic properties of pore-confined fluids.

We now describe the theoretical underpinnings of the model followed by calculations illustrating its use for both bulk and confined fluid situations.

Theoretical underpinnings of the equation of state

We consider a lattice gas with a fixed number of matrix (i.e., pore-blocked sites) randomly assigned throughout the structure. The remaining lattice sites are void spaces that may, or may not, be occupied by fluid particles. Nearest-neighbor fluid particles interact through a constant interaction energy parameter denoted by $\mathfrak{S}$ while solid matrix-fluid energetic interactions are represented by a binding site interaction parameter Γ . We consider a simple cubic lattice fluid in d dimensions and, for a system with matrix site density p ,

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we arrive at the following mean-field equation of state for the confined fluid, as described in detail elsewhere¹⁶

$$2\rho - 1 = \sum_{N=0}^z \frac{z!}{(z-N)!N!} (1-p)^{z-N} p^N \cdot \tanh \left[\frac{1}{2} \beta (4\mathfrak{S}\rho(z-N) + N\Gamma + \mu) \right] \quad (1)$$

To first-order in p (highly porous matrix) we find the equation¹⁶

$$(2\rho - 1) = (1 - zp) \tanh \left[\beta' (2z\rho + \frac{\mu'}{2}) \right] + zp \tanh \left[\beta' \left(2\rho(z-1) + \frac{1}{2}\Gamma' + \frac{\mu'}{2} \right) \right] \quad (2)$$

where

$$\beta' \equiv \beta\mathfrak{S} \quad (3)$$

$$\mu' \equiv \frac{\mu}{\mathfrak{S}} \quad (4)$$

$$\Gamma' \equiv \frac{\Gamma}{\mathfrak{S}} \quad (5)$$

$$T' \equiv \frac{1}{\beta'} = \frac{kT}{\mathfrak{S}} \quad (6)$$

The equation of state for **the bulk fluid** (i.e., $p = 0$) is given by

$$\rho = \frac{1}{2} \left[1 + \tanh \left[\beta' \left(2z\rho + \frac{\mu'}{2} \right) \right] \right] \quad (7)$$

In Eqs. 1–7 z is the lattice co-ordination number (equal to 6 in a 3-D fluid), ρ the fluid density, k is Boltzmann's constant γ' , μ' , Γ' are the *normalized* temperature, chemical potential and fluid-solid matrix interaction parameters, respectively. The normalizing parameter is the fluid–fluid interaction term designated by $\mathfrak{S}$ as seen in Eqs. 3–5. The conditions for the **critical point** in this system at the *low p (highly porous) limit* can be found using a perturbation analysis in conjunction with Eq. 2 arriving at the following equations¹⁷

$$\rho_c = \frac{1}{2} + \frac{1}{2} \tanh \left[\frac{\Gamma' - 2}{2z} \right] \left[z^2 - (z-1)^2 \sec^2 h^2 \left(\frac{\Gamma' - 2}{2z} \right) \right] p \quad (8)$$

$$T'_c = z \left[1 - p \left\{ z - (z-1) \sec^2 h^2 \left(\frac{\Gamma' - 2}{2z} \right) \right\} \right] \quad (9)$$

$$\mu'_c = -2z^2 \tanh \left[\frac{(\Gamma' - 2)}{2z} \right] p - 2z \quad (10)$$

In the **pure fluid bulk limit**, i.e., $p = 0$, Eqs. 8–10 yield the following theoretical predictions for the bulk fluid critical properties

$$\rho_c(p=0) = \frac{1}{2} \quad (11)$$

$$T'_c(p=0) = z \quad (12)$$

$$\mu'_c(p=0) = -2z \quad (13)$$

Application of the equation of state

Note that the physical basis of the equation of state leads to a representation of fluid properties, i.e., Eqs. 7–13 that first require a set of “subtle” transformations to be readily applicable to real fluids. We do this and then compare our model with the PR equation of state (itself based on empirical modifications to the van der Waals equation¹⁵). We use both bulk carbon dioxide and methane and subsequently investigate carbon dioxide adsorbed in a highly porous aerogel.

Equations 6 and 12 enable us to find a mapping between the model and the real fluid's critical properties. At the critical point of a fluid with *actual critical temperature* T_c , we have from Eqs. 6 and 12 that

$$\mathfrak{S} \equiv \frac{kT_c}{z} \quad (14)$$

In addition, the critical density in our model, given by Eq. 11 (half sites are filled), corresponds to the critical density of the pure fluid, generally known from experimental measurements so that the density transformation factor is given by

$$\alpha_\rho = \frac{\rho_c(\text{experimental data})}{\rho_c(\text{model}) = 0.5} \quad (15)$$

These results are the only information required for using the equation of state for predicting the density of the pure fluid at any given temperature and chemical potential using Eqs. 3–7.

Most experimental data, however, appear in the form of density-temperature-pressure co-ordinates. Since our equation naturally arises from an analysis in the grand canonical ensemble, during the transformation process we will need to establish a relationship between the chemical potential and the pressure to use these more common variables. Classical thermodynamics provides the key for doing this using the following identity for the pressure change with chemical potential at constant temperature between any two states 1 and 2

$$\Delta P_{1-2} = \int_{\mu'_1}^{\mu'_2} \rho(\Gamma', \mathfrak{S}, \beta') d\mu' \quad (16)$$

Using the model requires the following one-time steps to first establish the transformation factors between our model and the real fluid of interest:

1 For the fluid of interest with experimental critical properties ρ_c and T_c calculate $\mathfrak{S} = \frac{kT_c}{z}$ from Eq. 14 and from Eq. 15.

2 At the fluid T_c , we use the results of the previous step with Eq. 16 to find the chemical potential transformation factor for our model α_μ by iteratively doing this integral until the upper limit of the integral $\mu'_2 = \alpha_\mu \mu'_c (= -2z)$ gives a value of p_2 equal to the actual critical pressure of the fluid p_c . The bottom limit of the integral corresponds to the ideal gas limit ($\mu'_1 = -\infty$) where the pressure is zero.

Given these results, we are now in a position to use Eqs. 3–7 to calculate properties of the fluid with our equation-of-state model at any conditions of temperature and pressure of

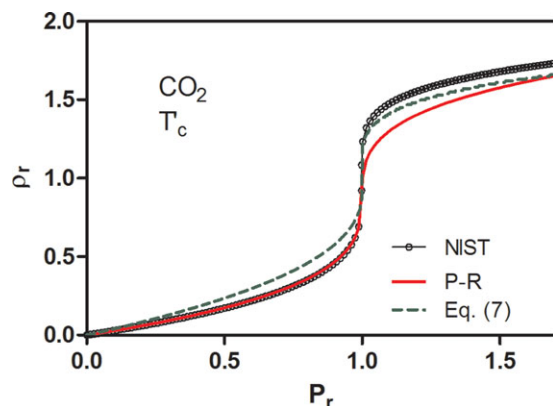


Figure 1. Reduced density (ρ_r) of bulk CO_2 as a function of reduced pressure (P_r) at the critical temperature.

Comparison of PR and Eq. 7 models to NIST data. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interest. Results are shown in Figures 1 and 2 for carbon dioxide and methane, comparing our model to the PR equation-of-state model and the NIST “data”.¹⁸

At lower pressures, the PR model follows the data better, while in the critical region both models have comparable accuracy with errors in the 5–14% range. However, as mentioned before, our equation of state seamlessly carries over into predictions of the pore-confined fluid’s thermodynamic properties which we now discuss in the following section.

Confined fluid

The crossover to the pore-confined fluid situation follows immediately from our equation of state, since this information is captured in Eqs. 2 and 8–10. We proceed with the following approach for fitting the equation to adsorption data. The reference model point is the critical point of the confined fluid, so that at experimental conditions we have that

$$T'_{\text{exp}} = \left(\frac{T_{\text{exp}}}{T_{c,\text{exp}}} \right) T'_c \quad (17)$$

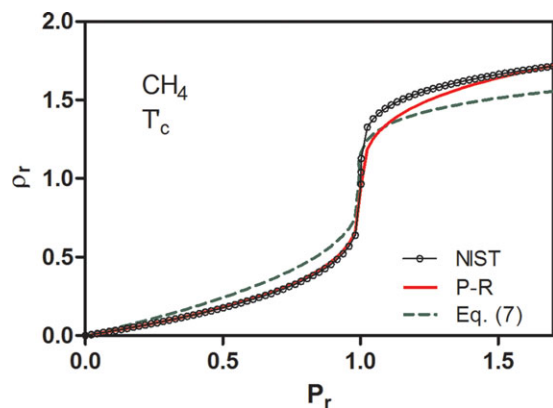


Figure 2. Reduced density (ρ_r) of bulk CH_4 as a function of reduced pressure (P_r) at the critical temperature.

Comparison of PR and Eq. 7 models to NIST data. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

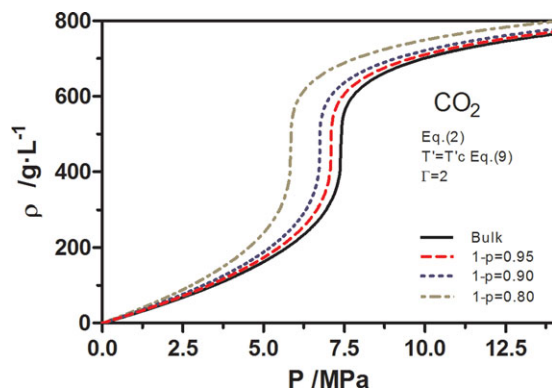


Figure 3. Adsorption isotherms, at the critical temperature, of confined CO_2 at three different porosities compared to the bulk density.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where the subscript *exp* refers to experimental data conditions. From Eq. 9, we see that the model’s theoretical T'_c for the confined fluid depends on both Γ' and p . We establish the reference fluid as having $\Gamma' = 2$, which is the unique maximum point of the critical temperature at any given p , and fit the single parameter $T_{c,\text{exp}}$ (for which data in porous systems are extremely rare) to the experimental data with the experimental reduced temperature T'_{exp} obtained from Eq. 17 using Eq. 16. The term in brackets in Eq. 17, thus, represents the experimental temperature departure from criticality of the confined fluid. In Figure 3, we show theoretical results with this approach for a fluid with carbon dioxide bulk properties in a confined system with a value $\Gamma' = 2$. Large enhancements in density are seen especially in the critical region. Moreover, there are large decreases in the predicted critical pressure values for the confined system. Finally, we fit our model, as described earlier, to recently published data¹⁹ for carbon dioxide adsorbed in a silica aerogel. The results are presented in Figure 4 for various values of porosity at a temperature of 308 K with the model providing a particularly good fit in the transition region using a porosity of 95% (we note that in the experimental article referred to the authors report a porosity of over 90%). Furthermore, we show model predictions of

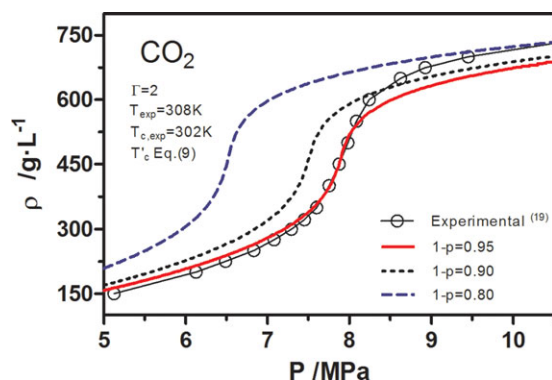


Figure 4. Adsorption isotherms, adjusted to an experimental temperature of 308 K, of confined CO_2 at three different porosities compared to the experimental adsorption of CO_2 on silica gel.¹⁹

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

density enhancements at other conditions for which experimental data are unavailable. These show large pressure shifts and density enhancements, demonstrating the value of having a theoretical equation-of-state model available for such purposes.

Conclusions

In this article, we have illustrated the use of a novel theoretically based mean field equation of state for thermodynamic property predictions in both bulk- and single-component adsorption systems. In the bulk fluid, we show comparisons between the model and the widely used Peng-Robinson cubic equation of state. These results demonstrate the two models to have comparable accuracy in these bulk fluids. However, our equation of state has an important advantage over the PR equation of state in that it seamlessly carries over into predictions of the pore-confined fluid's thermodynamic properties. We illustrate this point using recently published adsorption data in a carbon dioxide-silica aerogel system where our model is shown to provide an excellent representation of the experimental data. In the future, it would be useful to compare the model predictions with precise measurements of critical pressure shifts in a real pore-confined system, but such data are currently, to our best knowledge, unavailable.

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Notation

k = Boltzmann's constant
 n = molecule density in lattice gas
 p = density of particles in porous matrix
 P = pressure
 T = temperature
 z = lattice coordination number

Greek letters

β = $1/kT$
 μ = chemical potential
 Γ = fluid-solid coupling parameter in lattice gas
 $\mathfrak{Z}$ = nearest neighbor coupling parameter
 ρ = fluid density

Subscripts

c = critical property
 c, exp = experimental critical property

Superscripts

' = dimensionless property

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