



# Phase equilibrium of fluids confined in porous media from an extended Peng–Robinson equation of state



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## ABSTRACT

Fluid behavior in nanometric cavities and in bulk phases may be remarkably different but there is a dearth of simple analytical models that can predict such difference with a single set of parameters. In this work, commonly used cubic equations of state are extended to the modeling of fluids confined in porous media. A model based on the Peng–Robinson equation of state is used to study the phase equilibrium of pure fluids and mixtures confined in homogeneous and heterogeneous porous media. The problem is formulated as a multiphase equilibrium calculation because each kind of pore in a heterogeneous porous media has its own confinement effect and may contain one or more phases with unique properties. The specifications are the temperature, the total amount of each fluid component, the volume available for bulk phases, and the total volume of each kind of pore, so that the equilibrium condition is the minimum Helmholtz energy. The global phase stability test is executed to assess the need for phase additions. Results illustrate the potential of the model and of the multiphase equilibrium algorithm, by predicting different phase configurations under confinement. Each kind of pore may confine phases with very similar or very different densities and compositions. Furthermore, it is shown that the methodology of this work can predict the formation of transition regions like those of oil reservoirs.

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## 1. Introduction

Confinement in small scales changes fluid properties due to geometric constraints imposed on fluid molecules and interaction between these molecules and the pore walls (molecule–wall interaction). As an example, confinement may shift the phase transitions of a fluid, so that the confined fluid in equilibrium with a given bulk phase may be either a gas-like or a liquid-like phase, depending on the pore size and on the molecule–wall interaction energy [1,2]. In natural oil reservoirs, these effects give rise to transition regions known as GOC (gas–oil contact) and WOC (water–oil contact), where phases with different densities coexist at the same vertical level of the porous rock, due to its heterogeneity [3]. The occurrence of transition regions can be attributed to a variable capillary pressure through the reservoir because of different molecule–wall interactions in structurally or chemically distinct pores. The prediction of this phenomenon is important for oil recovery processes.

A detailed description of the local properties of confined fluids demands sophisticated approaches, such as molecular simulation techniques [4]. However, these techniques still have large computational cost, hindering their application to process simulation problems. Another approach, simplistic but with minimum computational cost, is the use of traditional adsorption isotherm models. Nevertheless, this approach combines different models for the bulk and adsorbed phases [5] and is unable to describe phase transition behavior between the confined and bulk states with a single set of parameters.

A third approach, developed more recently, is the use of an analytical equation of state that represents the main effects of confinement explicitly. This kind of model allows a continuous and self-consistent description of the fluid global properties as a function of the system dimensions. Besides, if the same equation of state is valid for bulk and confined fluids, existing algorithms for phase equilibrium calculations can be readily adapted to solve general adsorption equilibrium problems. Few models of this kind were proposed in the literature [6–8] and none of them is sufficiently accurate, in a large range of conditions, for application in engineering problems. One important application would be the prediction, with a single model, of the equilibrium distribution of oil and natural gas in the highly heterogeneous structures of shale reservoirs,

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in order to promote their recovery from these potential energy supplies [9].

In our previous work [10], an extension of the van der Waals equation of state was developed for modeling the behavior of confined fluids as an explicit function of pore size and of the molecule–wall interaction. Therefore, the same model could be used for both adsorbed and bulk phases, providing a consistent description of adsorption systems. This model describes different types of adsorption isotherms and several features of the confined fluid critical behavior [11] as predicted by theoretical work in the literature, like the emergence of a second critical point [12].

In this work, the same methodology used to extend the van der Waals model to confined fluids was applied to other cubic equations of state. The model obtained from the Peng–Robinson equation of state was used in a multiphase equilibrium calculation algorithm in order to investigate the phase configurations of pure fluids and mixtures confined in homogeneous and heterogeneous porous media.

## 2. Equations of state for confined fluids

The formulation of the model based on the van der Waals equation of state is discussed in detail elsewhere [10]. Here, we follow a similar modeling approach, which we summarize, focusing on the differences among the confined fluid models obtained from other equations of state.

Model development was guided by the generalized van der Waals theory [13,14]. The starting point is the canonical partition function ( $Q$ ), from which all thermodynamic properties of a closed system can be obtained:

$$Q(T, V, N_1, N_2, \dots, N_{NC}) = \prod_{i=1}^{NC} \left( \frac{q_i^{N_i}}{\lambda_i^{3N_i} N_i!} \right) V_f^N \exp \left( \int_{\infty}^T \frac{E_{conf}}{kT^2} dT \right)$$

where  $T$  is the temperature,  $V$  is the total volume,  $N$  is the total number of molecules in the fluid mixture,  $NC$  is the number of fluid components, index  $i$  denotes a component,  $q$  and  $\lambda$  are intramolecular and translational contributions, respectively,  $k$  is the Boltzmann constant,  $V_f$  is the free volume, and  $E_{conf}$  is the configurational energy. The system description is completed by assuming models for  $V_f$  and  $E_{conf}$ , which determine the repulsive and the attractive parts of the equation of state, respectively.

Assuming the classic mixing rule for the volume parameter of the equation of state,  $V_f$  is modeled by:

$$V_f = V - \sum_{i=1}^{NC} \left( \frac{N_i}{\rho_{max,i}} \right)$$

where  $\rho_{max,i}$  is the packing density of pure component  $i$ , whose dependence on pore size was obtained by fitting literature data [15] of hard spheres packed in cylinders:

$$\rho_{max,i} \sigma_i^3 = c_1 - c_2 \exp \left( c_3 \left( 0.5 - \frac{r_p}{\sigma_i} \right) \right) + c_4 \exp \left( c_5 \left( 0.5 - \frac{r_p}{\sigma_i} \right) \right)$$

where  $\sigma_i$  is the molecular diameter of component  $i$ ,  $r_p$  is the pore radius, and the fitting constants are  $c_1 = 1.158$ ,  $c_2 = 0.479$ ,  $c_3 = 0.621$ ,  $c_4 = 0.595$ , and  $c_5 = 4.014$ . For consistency with the packing density predicted by the equation of state which is being extended to confined fluids,  $\sigma_i$  must be calculated from the bulk volume parameter ( $b_i$ ) by [10]:

$$\sigma_i = \sqrt[3]{\frac{c_1}{N_{av}} b_i}$$

where  $N_{av}$  is the Avogadro number.

**Table 1**

Coordination number model for different bulk equations of state.

Equation of state	$N_{c,ij}^b$ Model
van der Waals	$cX_i\rho$
Redlich–Kwong	$\frac{d}{\sqrt{T}} \frac{x_i \rho_{max}}{\sqrt{\rho_{max,i} \rho_{max,j}}} \ln \left( 1 + \frac{\rho}{\rho_{max}} \right)$
Soave	$f_{S,ij}(T) \frac{x_i \rho_{max}}{\sqrt{\rho_{max,i} \rho_{max,j}}} \ln \left( 1 + \frac{\rho}{\rho_{max}} \right)$
Peng–Robinson	$f_{PR,ij}(T) \frac{x_i \rho_{max}}{\sqrt{\rho_{max,i} \rho_{max,j}}} \ln \left( \frac{1+(1+\sqrt{2})\rho/\rho_{max}}{1+(1-\sqrt{2})\rho/\rho_{max}} \right)$

Most of the cubic equations of state in common use differ only in the attractive part, which depends on the  $E_{conf}$  model. Considering that the pairwise interaction of fluid molecules (molecule–molecule interaction) occurs through a square well potential, the molecule–wall interaction occurs through another square well potential, and the interaction potentials of all fluid components are pairwise additive,  $E_{conf}$  was modeled by [10]:

$$E_{conf} = - \sum_{i=1}^{NC} \sum_{j=1}^{NC} \left( \frac{N_j}{2} N_{c,ij} \varepsilon_{ij} \right) - \sum_{i=1}^{NC} (N_i F_{p,i} \varepsilon_{p,i})$$

where  $\varepsilon_{ij}$  is the intermolecular interaction energy between components  $i$  and  $j$ ,  $\varepsilon_{p,i}$  is the interaction energy between one molecule of component  $i$  and the entire pore wall,  $N_{c,ij}$  is the coordination number (i.e., the number of molecules of component  $i$  that coordinate with a central molecule of component  $j$ ), and  $F_{p,i}$  is the fraction of the confined molecules in the range of the pore wall attractive field. In the previous equation, the first term on the right hand side accounts for molecule–molecule interactions and the second one accounts for molecule–wall interactions. The term  $F_{p,i}$  is intended to represent the distribution of fluid molecules inside the pore, which depends on temperature, fluid density, and geometric features of the system. This term was modeled by an empirical expression that satisfies some physical limits expected for the system [10]:

$$F_{p,i} = F_{pa,i} + (1 - F_{pa,i}) \left( 1 - \exp \left( - \frac{\varepsilon_{p,i}}{kT} \right) \right) \left( 1 - \frac{x_i \rho}{\rho_{max,i}} \right)^{\theta_i}$$

where  $\rho$  is the fluid density,  $x_i$  is the mole fraction of component  $i$ ,  $F_{pa,i}$  is the value of  $F_{p,i}$  for random distribution of the fluid molecules inside the pore:

$$F_{pa,i} = \frac{(r_p - \sigma_i/2)^2 - (r_p - \sigma_i/2 - \delta_{p,i})^2}{(r_p - \sigma_i/2)^2}$$

$\theta_i$  is a geometric term:

$$\theta_i = \frac{r_p}{\delta_{p,i} + \sigma_i/2}$$

and  $\delta_{p,i}$  is the square well width of the molecule–wall interaction potential of component  $i$ . The coordination number was also modeled by an empirical expression:

$$N_{c,ij} = N_{c,ij}^b \left( 1 - \frac{2}{5} \frac{\sigma_{ij}}{r_p} \right)$$

where  $N_{c,ij}^b$  is the bulk coordination number,  $\sigma_{ij}$  is the mean molecular diameter for components  $i$  and  $j$ , and the term in parenthesis accounts for the coordination number decrease with pore size reduction. The  $N_{c,ij}^b$  expression is specific for each bulk fluid equation of state and depends on the mixing rules adopted. Table 1 shows the underlying  $N_{c,ij}^b$  expressions for different bulk models, assuming classic mixing rules. In these expressions,  $c$  and  $d$  are constants,  $f_{S,ij}$  and  $f_{PR,ij}$  are functions of temperature, and  $\rho_{max}$  is

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