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Critical temperature shift modeling of confined fluids using pore-size-dependent energy parameter of potential function

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The behavior and critical properties of fluids confined in nanoscale porous media differ from those of bulk fluids. This is well known as critical shift phenomenon or pore proximity effect among researchers. Fundamentals of critical shift modeling commenced with developing equations of state (EOS) based on the Lennard–Jones (L–J) potential function. Although these methods have provided somewhat passable predictions of pore critical properties, none represented a breakthrough in basic modeling. In this study, a cubic EOS is derived in the presence of adsorption for Kihara fluids, whose attractive term is a function of temperature. Accordingly, the critical temperature shift is modeled, and a new adjustment method is established in which, despite previous works, the bulk critical conditions of fluids are reliably met with a thermodynamic basis and not based on simplistic manipulations. Then, based on the fact that the macroscopic and microscopic theories of corresponding states are related, an innovative idea is developed in which the energy parameter of the potential function varies with regard to changes in pore size, and is not taken as a constant. Based on 94 available data points of critical shift reports, it is observed that despite L-J, the Kihara potential has sufficient flexibility to properly fit the variable energy parameters, and provide valid predictions of phase behavior and critical properties of fluids. Finally, the application of the proposed model is examined by predicting the vapor-liquid equilibrium properties of a ternary system that reduced the error of the L–J model by more than 6%.

Abbreviations

List of symbols

- *a_k* Kihara spherical core radius
- a_k^* Reduced Kihara size parameter
- a_{PR}^{r} Peng-Robinson constant
- a_{vdW} Van der Waals constant
- A Transverse pore reduced area
- B(T) Second virial coefficient
- *b*_{PR} Peng-Robinson constant
- b_{vdW} Van der Waals constant
- C Coefficient
- E Internal energy
- f(T) Free energy of ideal gas F Helmholtz free energy
- F Helmholtz free energy H Hermite function
- I Integral numerical solution
- k Boltzmann constant
- L Length
- m Coefficient
- MW Molecular weight
- n Coefficient
- N System particles number

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- N_A Avogadro constant
- Component of pressure tensor Pii
- $\overrightarrow{\frac{P}{P}}$ System pressure
- Pressure tensor
- P_c Bulk critical pressure
- r Distance between molecular centers
- Pore size
- r_p S T Entropy
- System temperature
- Reduced temperature
- Bulk critical temperature Capillary critical temperature
- $\begin{array}{c} T^* \\ T_c \\ T_{cc} \\ T_{cp} \\ T_r \\ U \end{array}$ Pore critical temperature
- Bulk reduced temperature
- Internal energy
- $U(r_{12})$ Potential function
- Molar volume ν
- V System volume

Greek symbols

- Coefficient $\beta : 1/kT$ α
- Г Gamma function
- Coefficient γ
- δ_p Adsorption thickness
- Kihara energy parameter $\varepsilon_k : \varepsilon/k$ ε
- Bulk ε_k ε_{kh}
- ε_k In pores ε_{kp}
- Tensor of volume deformation ϵ_{ii}
- Coefficient λ
- Viscosity μ
- Size parameter σ
- Acentric factor ω

Subscripts

- с Critical
- ii Direction of a tensor's components
- k Kihara
- LJ Lennard-Jones
- Pore
- PR Peng-Robinson
- Van der Waals vdW

In recent years, countless research works have been conducted in order to understand and evaluate the phase behavior of fluids confined in molecular scale pores, especially hydrocarbons, due to the growing demand for production from unconventional oil and gas reserves. Phase behavior and thermodynamics of confined fluids have a notable deviation from their corresponding bulk behavior. Experimental measurements¹⁻⁴ have revealed that the thermodynamic and physicochemical properties of fluids, such as their critical properties, considerably shift when they are confined in a porous medium with pore radius of molecular scale. This phenomenon is originally named and known in the literature as Critical Shift or Pore Proximity Effect. Even its applicability has been investigated in several other research areas, such as nanofluidic chipset technologies⁵. Because of the occurrence of critical shift in confined media, applying the bulk properties of matters undoubtedly leads to poor results when calculating vapor-liquid equilibrium (VLE) properties of their confined state.

Various analytical and numerical methods have been examined to predict and model the above theory for pure normal fluids, e.g., developed microscopic van der Waals (vdW) equation of state (EOS) in a similar previous study⁶, molecular dynamics simulation (MD)⁷, density functional theory⁸, lattice Boltzmann method (LBM)⁹, scaled particle theory (SPT or RFL)¹⁰, and different classes of Monte Carlo simulations¹¹⁻¹⁹.

Numerical approaches are frequently inconvenient to be applied to a different scope since they are accompanied by numerous limitations and great complexity. Having a theoretical and thermodynamic basis, the mentioned modified vdW EOS has been widely used because of its compatibility with experimental values on the one hand, and its ease of use on the other. Such a convenience would be much preferable to implementing timeconsuming and inconvenient huge numerical simulation for every research case. The EOS method has been developed using the Lennard–Jones (L–J) potential function with two adjustable parameters ($\sigma_{LJ}, \varepsilon/k$) whose values can be determined via least-square fitting of thermodynamic properties²⁰. A three-parameter potential function (like Kihara), nevertheless, is supposed to perform much better due to possessing the ability to provide more flexible modeling and accurate predictions²¹.

In addition, fluid adsorptions and their huge impacts on phase behavior cannot be ignored^{22,23}. A multi-layer film of fluid is always absorbed by pore walls and its contribution to fluid characteristics is great enough to be considered, because, in nanoscale (confined) porous media, the wall-molecule interactions are not insignificant anymore as they are in bulk state. In this regard, analytical²²⁻²⁴ and numerical²⁵⁻²⁸ research works have been conducted to include the adsorption phenomenon. Although experimental measurements are always highly reliable and give direct understanding of fluid properties, they are greatly time-consuming and require highly expensive setups to study confined porous media. Moreover, it is quite difficult to establish an apparatus that could last under extreme conditions of high pressure and temperature²³.

Over the last few years, various measures have been taken to enhance the confinement modeling of fluids; yet, no fundamental and analytical development was presented except for the previous original model of L–J⁶. Other fellow researchers have merely manipulated numbers and coefficients through curve fittings^{29–32}. In several works, furthermore, the mentioned L-J approach has been repeated with corrections of the theory's coefficients^{33–35}. These numerical enhancements strongly depend on the available data sets of one specific compound, and are probably inappropriate for comprehensive applications. Such uncertainty even led to developing exclusively curve-fitted correlations for substances like CH_4 , C_2H_6 , and $CO_2^{4,31}$.

Despite Lennard–Jones (previous works), the Kihara potential function has three adjustable parameters and incorporates the hard-impenetrable core of a molecule into the modeling via its third potential parameter, a_k ³⁶. However, there is no limitation for two approaching molecules in the L-J model and they can completely penetrate. Kihara successfully fits thermodynamic data, specifically the second virial coefficient for different types of fluids. The L-J potential, in contrast, performs weaker in lower temperatures, whilst the flexibility of the Kihara potential makes it much easier to have a perfect fitting²⁰.

In the current study, first the theory is presented where the vdW EOS is derived for Kihara fluids as a generalized format of the Lennard–Jones. Despite previous works, the energy integral is solved exactly and without any approximations, leading to an exclusive solution for each fluid at any specific temperature. Second, an innovative idea is developed for the very first time in which the energy parameter of the potential is taken as a function of pore radius and is not constant. Third, this notion is supported by a collection of 94 critical shift data points available in the literature–80% for model development (training) and 20% for model verification (testing)–so as to make the phase behavior calculations much more reliable. Forth, the occurrence of capillary condensation is investigated for the van der Waals and Peng-Robinson equations of state when coupled with the Lennard–Jones and Kihara potential functions. Finally, the application of our study is investigated by phase behavior calculations in the last section where the performance of the proposed model is examined by calculating the vapor–liquid equilibrium (VLE) properties of a ternary mixture, and its results are compared to those of the L–J model and the experimental values. Figure 1 presents the general sketch of the studied problem in this work.





Theory

How to better model the critical temperature of confined fluids? At the first step, the conventional vdW EOS must be modified in order to describe the confinement phenomenon. Although a simple cubic EOS, the vdW model is properly able to predict the vapor-liquid equilibrium (VLE) conditions and phase behavior properties of either pure or mixing fluids. As shown in Fig. 2, we consider a Cartesian pore model ($L_x = L_y$ and $L_z = \infty$) consisting of confined fluids for which the pressure \vec{P} is a diagonal tensor with components p_{ii} , (i = x, y, z). The internal energy is given by³⁷,

$$dE = TdS - \sum_{i} p_{ii} d\epsilon_{ii} V \tag{1}$$

where the term $-\sum_i p_{ii} d\epsilon_{ii} V$ shows how much work the internal tension has done under a specific deformation $d\epsilon_{ii}$ of volume *V*. From the Helmholtz free energy F = E - TS we have³⁷

$$dF = -SdT - \sum_{i} p_{ii} d\epsilon_{ii} V \tag{2}$$

Therefore the Helmholtz free energy of a system including N particles interacting by a pair potential $U(r_{12})$ can be derived from the perturbation theory as⁶

$$F = f(T) - \frac{kTN^2}{2V^2} \iint \left(e^{-\beta U(r_{12})} - 1 \right) dV_1 dV_2$$
(3)

where f(T) is the free energy of ideal gas; k is the Boltzmann constant; and β is 1/kT. The term $e^{-\beta U(r_{12})} - 1$ is often called the Mayer function. Here, we utilize the Kihara potential with three adjustable parameters for the interaction between particles. But why Kihara? Its formulation (Eq. 4) is the generalized format of the Lennard–Jones; hence, L-J would be a special case of Kihara and its corresponding properties will be readily in hand when the Kihara hard core is ignored.

Despite the Lennard–Jones theory in which two molecules can fully interpenetrate provided that they have enough energy²⁰, in the Kihara model, the repulsion interaction in the rigid spherical core is split into two parts; a rigid core and an outer soft spherical repulsion region³⁸. We suppose soft-penetrable electron clouds surround a hard-impenetrable core. Given that, the model's mathematical expression would be²⁰,

$$U(r_{12}) = \begin{cases} \infty & r < 2a_k \\ 4\varepsilon \left[\left(\frac{\sigma_k - 2a_k}{r - 2a_k} \right)^{12} - \left(\frac{\sigma_k - 2a_k}{r - 2a_k} \right)^6 \right] & r \ge 2a_k \end{cases}$$
(4)

where a_k is the radius of the spherical core; ε is the depth of the energy well (herein we employ $\varepsilon_k = \varepsilon/k$ instead of ε); and σ_k is the collision diameter, i.e., the distance *r* between molecular centers when $U(r_{12}) = 0$. The intermolecular distance can go from $r_{12} = 2a_k$ (where the repulsion force is infinity) to $r_{12} = \infty$.

Given Eq. (3), the standard vdW equation can be derived by integrating over an infinite volume. For a finite volume, the same procedure could be applied by splitting the integral into two regions, $2a_k < r_{12} < \sigma_k$ and $r_{12} > \sigma_k$:

$$F = f(T) - \frac{kTN^2}{2V^2} \left[\iint_{2a < r_{12} < \sigma} \left(e^{-\beta U(r_{12})} - 1 \right) dV_1 dV_2 + \iint_{r_{12} > \sigma} \left(e^{-\beta U(r_{12})} - 1 \right) dV_1 dV_2 \right]$$
(5)



Figure 2. Schematic of a nano-scale pore in the Cartesian coordinates.

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When the intermolecular distance is less than σ_k , the value of $U(r_{12})$ increases drastically to infinity; hence, we can utilize the assumption $e^{-\beta U(r_{12})} \cong 0$. Then the energy is given by,

$$F = f(T) + \frac{kTN^2}{V}b - \frac{kTN^2}{2V^2} \iint_{r_{12} > \sigma} \left(1 - e^{-\beta U(r_{12})}\right) dV_1 dV_2$$
(6)

where $b = \frac{2\pi}{3} (\sigma_k^3 - (2a_k)^3)$ and $V = L_x L_y L_z$ in which $L_x = L_y = L$ and $L_z = L_z$ for a pore model in the Cartesian coordinates. In spite of what has been done for the L–J⁶, here the latter integral will be solved exactly, without any simplifying assumption (henceforth referred to as "**exact solution**" for simplification). The reason is that the approximation term in the region $r_{12} > \sigma_k$, i.e., $e^{-\beta U(r_{12})} \cong 1 - \beta U(r_{12})$, is in fact a good and close approximation for the L–J model, while such a substitution could not necessarily be made for the Kihara. Considering CO₂ at 300 K an example, this assertion is well supported for both potentials in Fig. 3 where the light-colored region of L–J is insubstantial compared to that of Kihara. This difference is even more intense at lower temperatures, leaving no other alternatives except for the exact solution.

The semi-analytical solution of the latter integral is as follows,

$$\frac{1}{V} \iint_{r_{12} > \sigma} \left(1 - e^{-\beta U(r_{12})} \right) dV_1 dV_2 = \sigma_k^3 \times I(A, a_k^*, T^*)$$
(7)

$$I(A, a_k^*, T^*) = C_0(a_k^*, T^*) + \frac{C_1(a_k^*, T^*)}{\sqrt{A}} + \frac{C_2(a_k^*, T^*)}{A}$$
(8)

where $A = L_x L_y / \sigma_k^2$ is the reduced area of the square cross section of the pore, $a_k^* = 2a_k / \sigma_k$ is the reduced Kihara parameter, $T^* = T/\varepsilon_k$ is the reduced temperature, $I(A, a_k^*, T^*)$ is the numerical solution to the integral, and C_0 to C_2 are component- and temperature-dependent coefficients. In the L-J model, there is just one set of coefficients (C constants) used for all matters, whereas in this study, the numerical solution differs for any specific component represented by its a_k^* . Figure 4 shows the 3D diagram of $I(A, a_k^*, T^*)$ versus A and T* for three different values of a_k^* . For larger molecules, or heavier substances, a_k^* is greater in magnitude and the changes in the value of numerical solution will be more dramatic with respect to T* or A. Note that Fig. 4 is the result of super timeconsuming computational processes of numerical solution to the integration in Eq. (7), and is achieved with the help of Gauss-Legendre quadrature method to obtain the most possible exact outcomes.

For a bulk fluid, A goes to infinity and $I(A, a_k^*, T^*)$ must be subsequently equal to C_0 . Therefore, if we take the integration of Eq. (7) from σ_k to ∞ , the analytical expression of C_0 will be obtained. In this case, C_0 and the second virial coefficient will share similar definitions and we can derive a formula for C_0 as a function of B(T). Based on the partition function theory, the second virial coefficient of a bulk fluid is defined as³⁹

Based on the partition function theory, the second viral coefficient of a bulk fluid is defined as³⁹

$$B(T) = 2\pi N_A \int_0^\infty \left(1 - e^{-\beta U(r_{12})} \right) r^2 dr.$$
 (9)

For the very first time, we present the exact analytical solution of Eq. (9) for Kihara fluids,







Figure 4. 3D diagram of $I(A, a_k^*, T^*)$ versus the reduced area and temperature for different values of the reduced Kihara parameter.

$$B(a_{k}^{*}, T^{*}) = 2\pi N_{A} \sigma_{k}^{3} (1 - a_{k}^{*})^{3} \times \left(\frac{-\left(\frac{1}{T^{*}}\right)^{\frac{1}{4}}}{12\sqrt{\pi}} \left(\Gamma\left[-\frac{1}{4}\right]\Gamma\left[\frac{1}{4}\right]\right) H_{\frac{1}{2}}\left[-\sqrt{\frac{1}{T^{*}}}\right] + \frac{3 \times a_{k}^{*}\left(\frac{1}{T^{*}}\right)^{\frac{1}{6}}}{\sqrt{\pi}\left(1 - a_{k}^{*}\right)} \left(\Gamma\left[\frac{5}{6}\right]\Gamma\left[\frac{4}{3}\right]\right) H_{\frac{1}{3}}\left[-\sqrt{\frac{1}{T^{*}}}\right] + \frac{a_{k}^{*2}\left(\frac{1}{T^{*}}\right)^{\frac{1}{2}}}{\sqrt{\pi}\left(1 - a_{k}^{*}\right)^{2}} \left(\Gamma\left[\frac{11}{12}\right]\Gamma\left[\frac{5}{12}\right]\right) H_{\frac{1}{6}}\left[-\sqrt{\frac{1}{T^{*}}}\right] \right)$$
(10)

in which H_n is the Hermite function of degree *n* and Γ is the Gamma function. Setting $a_k^* = 0$, the last two terms in the parenthesis will be removed and we are given by the analytical formula of the second virial coefficient for the Lennard–Jones fluids. This equation is obtained with the aid of Wolfram Mathematica version 12.1⁴⁰.

After series of manipulation (more details in Supporting Information 1), the analytical equation of C_0 is

$$C_0(a_k^*, T^*) = \frac{2B(a_k^*, T^*)}{\sigma_k^3 \times N_A} - 2b^*$$
(11)

where $b^* = (2\pi/3) \left(1 - a_k^{*3}\right)$. The coefficients C_1 and C_2 can be written as a function of C_0 with R^2 of 0.9997, as follows,

$$C_i(a_k^*, T^*) = m_i C_0(a_k^*, T^*) + n_i i = 1, 2$$
(12)

in which

$$m_i = \frac{(\gamma_1)_i + (\gamma_2)_i \times a_k^*}{1 + (\gamma_3)_i \times a_k^* + (\gamma_4)_i \times a_k^{*2}}$$
(13)

$$n_{i} = (\lambda_{1})_{i} + (\lambda_{2})_{i} \times a_{k}^{*} + (\lambda_{3})_{i} \times a_{k}^{*2}.$$
(14)

The constants γ and λ for each coefficients m and n are presented in Table 1.

The Helmholtz free energy of a confined fluid is formulated by Eq. (15) obtained by applying the ideal gas free energy and considering the limited compressibility of matters via substituting $\ln V - (\frac{N}{V})b = \ln(V - Nb)$.

$$F = f(T) - NkTln(V - Nb) + \frac{kTN^2}{2V}\sigma_k^3 \times I(A, a_k^*, T^*)$$
(15)

In the vdW theory, a molecule's volume (the volume excluded from the system) is designated by the variable b which represents the available space to molecules for overlap. With this definition, other molecules will have an accessible volume of V - Nb to move in. This is the backbone of the idea laying behind the substitution used in Eq. (15), which is obviously independent of the applied potential function.

	γ 1	γ2	γ3	γ_4
m_1	- 1.24981	1.757866	-1.41068	0.193374
<i>m</i> ₂	0.390334	-0.63274	-1.67588	0.534595
	λ_1	λ_2		λ3
n_1	6.559926	- 19.3229		17.89491
<i>n</i> ₂	- 5.89906	17.97434		- 17.1227

Table 1. Values of constants γ and λ for m and n coefficients.

As Fig. 2 shows, a cross-section confinement occurs in an axially infinite pore for which the axial (P_{zz}) and transverse $(P_{xx} \text{ and } P_{yy})$ components of the pressure tensor are as follows,

$$p_{ii} = -\frac{1}{V} \frac{\partial F}{\partial \epsilon_{ii}} \tag{16}$$

$$P_{xx} = P_{yy} = -\frac{\sigma_k^2}{L} \frac{\partial F}{\partial A}, P_{zz} = -\frac{\sigma_k^2}{A} \frac{\partial F}{\partial L}$$
(17)

Using Eqs. (17), and applying (15(, the axial and transverse components are given by Eqs. (18) and (19).

$$P_{xx} = P_{yy} = \frac{NkT}{V - Nb} - \frac{kTN^2}{2V^2} \sigma_k^3 \left[-C_0(a_k^*, T^*) - \frac{3}{2} \frac{C_1(a_k^*, T^*)}{\sqrt{A}} - \frac{2C_2(a_k^*, T^*)}{A} \right]$$
(18)

$$P_{zz} = \frac{NkT}{V - Nb} - \frac{kTN^2}{2V^2} \sigma_k^3 \left[-C_0(a_k^*, T^*) - \frac{C_1(a_k^*, T^*)}{\sqrt{A}} - \frac{C_2(a_k^*, T^*)}{A} \right]$$
(19)

Clearly, when $A \to \infty$, the bulk vdW equation is derived and $P_{xx} = P_{yy} = P_{zz}$. In reduced coordinates, Eqs. (18 and 19) can be written as,

$$P_{xx}^* = P_{yy}^* = \frac{T^*}{\nu^* - b^*} - \frac{T^*}{\nu^{*2}} \left[-\frac{C_0(a_k^*, T^*)}{2} - \frac{3}{4} \frac{C_1(a_k^*, T^*)}{\sqrt{A}} - \frac{C_2(a_k^*, T^*)}{A} \right]$$
(20)

$$P_{zz}^{*} = \frac{T^{*}}{v^{*} - b^{*}} - \frac{T^{*}}{v^{*2}} \left[\underbrace{-\frac{C_{0}(a_{k}^{*}, T^{*})}{2} - \frac{1}{2} \left(\frac{C_{1}(a_{k}^{*}, T^{*})}{\sqrt{A}} + \frac{C_{2}(a_{k}^{*}, T^{*})}{A} \right)}_{-I(A, a_{k}^{*}, T^{*})/2} \right]$$
(21)

where $P^* = P\sigma_k^3 / \varepsilon [Pa.m^3.J^{-1}]$; $T^* = kT/\varepsilon [J.K^{-1}.K.J^{-1}]$; $v^* = (V/N)\sigma_k^{-3} [m^3.m^{-3}]$; and $b^* = b\sigma_k^{-3} [m^3.m^{-3}]$. Equations (20 and 21) have a format akin to the standard vdW cubic EOS, but we exclusively observe that the attractive term is a function of temperature, and this would not be possible except with the exact solution of Eq. (6).

From the theory of corresponding states and the continuity principle of gaseous and liquid phases, the following conditions are required for vdW type EOSs at the critical point⁴¹:

$$\left(\frac{\partial P_{zz}^*}{\partial v^*}\right)_{T^*=T_c^*} = \left(\frac{\partial^2 P_{zz}^*}{\partial v^{*2}}\right)_{T^*=T_c^*} = 0$$
(22)

Applying the requirements on Eq. (21), we can establish the following relations with which the critical properties of a Kihara fluid can be obtained:

$$I(A, a_k^*, T_c^*) = C_0(a_k^*, T_c^*) + \frac{C_1(a_k^*, T_c^*)}{\sqrt{A}} + \frac{C_2(a_k^*, T_c^*)}{A} = -\frac{27}{4}b^*$$
(23)

$$P_c^* = \frac{T_c^*}{8b^*}$$
(24)

$$v_c^* = 3b^* \tag{25}$$

Not only Eqs. (23 and 24) reveal a shift in critical temperature and pressure of fluids, but they imply that in spite of the L-J critical shift equations⁶, it is not feasible to directly calculate the critical temperature. Herein the focus is on the critical temperature shift of substances.

At the critical point and based on Eq. (21), the EOS will possess the following format:

$$P_c^* = \frac{T_c^*}{v_c^* - b^*} - \frac{T_c^* \left(-I\left(A, T_c^*, a_k^*\right)/2\right)}{v_c^{*2}}$$
(26)

Rearranging the relation and replacing $v_c^* = Z_c T_c^* / P_c^*$, we get the below cubic relation,

$$Z_{c}^{3} - \left(1 + \frac{P_{c}^{*}}{T_{c}^{*}}b^{*}\right)Z_{c}^{2} + \frac{P_{c}^{*}}{T_{c}^{*}}\left(-\frac{I(A, T_{c}^{*}, a_{k}^{*})}{2}\right)Z_{c} - \frac{P_{c}^{*2}}{T_{c}^{*2}}\left(-\frac{I(A, T_{c}^{*}, a_{k}^{*})}{2}\right)b^{*} = 0$$
(27)

which is the original vdW EOS provided we substitute $b^* = T_c^*/8P_c^*$ and $I(A, T_c^*, a_k^*) = (-27/4)b^*$. Therefore, regardless of pore size and the critical shift effect or the presence of temperature in the attractive term, Eq. (27) has always the exact single root of vdW, i.e., 3/8.

Being the focal point of this study, Eq. (23) hints that the numerical solution to Eq. (7) at the critical point $-I(A, a_k^*, T_c^*)$ – always owns a constant value of $-27/4 \times b^*$, which is independent of the critical temperature or pore area (*A*), and is only a function of fluid type (a_k^*) . For a detailed inspection, Fig. 5 provides a representation of the essence of Eq. (23) where Fig. 4 and the term $-27/4 \times b^*$ come together, as identified by the black dashed line. Their intersections represents the values of T_c^* at various pore radii which levels out sooner for larger molecules (Fig. 5b) than the lighter ones (Fig. 5a).

As discussed earlier, Eq. (23) must be solved numerically to find the critical temperature at the desired pore radius using the Kihara parameters gained from fluid's properties⁴². Figure 6 demonstrates the dimensionless diagram of numerically calculated values of T_c^* for a limited range of dimensionless parameters A and a_k^* . Yet, in the L-J model, T_c^* merely depends on A (or pore size) and the effect of fluid type is not included⁴³.

To calculate the critical temperature of a confined fluid, whether of Kihara or L–J type, one should have σ_k , a_k , r_p , and ε_k known. Then a_k^* and A are given to Eq. (23) as inputs and T_c^* will be obtained after rooting find. Alternatively, Fig. 6 is available as a dimensionless chart and can be employed for light and semi-heavy molecules as well as the L–J type fluids within the nanometric pore sizes. Note that, in this figure, the $a_k^* = 0$ curve represents the L–J fluid type, if the exact solution procedure is followed with the Lennard–Jones potential function.

It should be noted that all the aforementioned calculations can correspondingly be applied to nano-scale pores in cylindrical coordinates (Fig. 7) where pores are infinite over the Z direction and $A = \pi (r_p/\sigma_k)^2$.

The molecule-wall interactions cannot be ignored in molecular-scale studies; such interactions lead to a layer of fluid's molecules stuck on the surface of pore walls, known as adsorption thickness (Fig. 7). In this regard, there will be a slight change to the definition of dimensionless area (A) as follows:

$$A = \pi \left(\frac{r_p - \delta_p}{\sigma_k}\right)^2 \tag{28}$$

where δ_p is the adsorption thickness for which here we employ the values Zhang et al.²³ have reported in their work. In this study, instead of a logarithmic function proposed in their paper, a rational model as Eq. (29) is used for least square fitting that results in less deviation:

$$\delta_p = \frac{a + b \times r_p}{1 + c \times r_p + d \times r_p^2} \tag{29}$$

in which r_p and δ_p are both in nm. Moreover, a, b, c, and d are coefficients whose values are listed in Table 2 for N2, CO2, and normal hydrocarbons from C1 to C10. Figure 8 shows the measured²³ and fitted values of δ_p . Furthermore, the following expressions may be used for normal alkanes based on the values presented in Table 2:

$$a = 0.12 \ln \omega + 1.0495 R^2 = 0.9235 \tag{30}$$

$$b = 0.0225 \ln \omega + 0.1332 R^2 = 0.8675$$
(31)

$$c = -1.0654\omega^2 + 0.1643\omega + 0.6555R^2 = 0.7315$$
(32)

$$d = 6.3464 \times 10^{-6} \ln \omega - 5.9508 \times 10^{-6} R^2 = 0.8454$$
(33)

Considering the wall-molecule interactions, the critical shift phenomena is now modeled better and more realistic than the previous work⁶ which was developed for neutral pore walls.

Adjustment: the bulk critical conditions must be met in $A = \infty$. As we discussed earlier, Eq. (23) is the key formula of this research. For any given values of Kihara parameters, this formula provides the critical temperature of a fluid under confinement at any desired pore radius. The problem is, however, that potential function parameters are derived through thermodynamic data fitting of different sources. Therefore, a calculated set of parameters from one data set, e.g. B(T), may (and will) differ from those of another (e.g. μ). This occurs



Figure 5. Diagram of the integral numerical solution, $I(A, T^*, a_k^*)$, versus T^* for two types of fluids; (**a**) $a_k^* = 0.1$ representing light-weight molecules, and (**b**) $a_k^* = 0.5$ representing mid-weight molecules. Dashed line denotes the value of the numerical integration at the critical point, $I(A, T_c^*, a_k^*)$, and its intersections with diagram curves determine the value of T_c^* at each pore size.

because potential functions are merely a representative and approximation of the real potential behavior of two interactive molecules. Only for a true potential there is one unique set of parameters obtained from different properties of the same fluid²⁰.

Inserting any precalculated Kihara (or L–J) parameters^{21,42,44,45} in Eq. (23), the bulk critical temperature (T_c) (and subsequently the bulk critical pressure (P_c) from Eq. (24)) is expected to be achieved when A approaches infinity: $I(A, a_k^*, T_c^*) = C_0(a_k^*, T_c^*)$. Nevertheless, there is a remarkable deviation for both Kihara and L-J potential functions when calculating bulk T_c , as listed in Table 3.

Hence, the model must be somehow **adjusted** in that regard. An adjustment method for the Lennard–Jones potential function was presented by Zarragoicoechea and Kuz⁴³ applying a rough approximation to Eq. (6). While broadly drawing the attention of researchers, that adjustment method seems to be a numerical correlation and lacks a thermodynamic basis. Here we propose a new adjustment procedure with which the mentioned bulk state conditions will be satisfied with a thermodynamic basis, and there will be no need for auxiliary equations. To this end, the potential function's parameters will be manipulated until Eqs. (23 and 24) result in the critical properties of a fluid in the macroscopic state.







Figure 7. Schematic of a nano-scale pore in cylindrical coordinates including the adsorption thickness effect.

							1	1				
	N2	CO2	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
а	0.4441	0.8646	0.4848	0.7678	0.8601	0.9029	0.9543	0.8985	0.9178	0.9136	0.9139	0.9218
b	0.0239	0.1009	0.0288	0.0748	0.0949	0.1051	0.1257	0.1033	0.1080	0.1062	0.1071	0.1096
с	0.6594	0.7955	0.6520	0.6465	0.6687	0.6338	0.7231	0.5655	0.5526	0.5209	0.5203	0.5048
$d(\times 10^{-5})$	- 3.849	-0.435	- 3.695	- 1.809	- 1.462	- 1.620	-0.867	- 1.535	- 1.422	-1.371	- 1.143	- 1.393
R ²	0.9997	0.9999	0.9996	0.9997	0.9998	0.9997	0.9999	0.9996	0.9996	0.9996	0.9995	0.9995

Table 2. Values of coefficients in the adsorption thickness equation (Eq. 29).

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Approaching the cross section to infinity and rewriting Eqs. (23 and 24), we have (more details in Supporting Information 2):

$$\frac{2}{N_A} B\left(a_k^*, T/\varepsilon_k\right)\Big|_{T=T_C} = -\frac{19}{32} \times \frac{kT_c}{P_C}$$
(34)



Figure 8. Measured 23 and fitted values of adsorption thickness.

	Kihara				Lennard-Jones							
	Set 1 ⁴²		Set 245		Set 1 ²¹		Set 244					
	$T_c[K]$	Error %	$T_c[K]$	Error %	$T_c[K]$	Error %	$T_c[K]$	Error %				
CH ₄	178.30	6.43	171.56	9.97	148.40	22.12	153.93	19.22				
C ₂ H ₆	369.76	21.11	-	-	201.65	33.95	252.40	17.33				
n-C ₄ H ₁₀	446.84	5.11	-	-	232.40	45.33	308.45	27.44				
n-C ₅ H ₁₂	504.52	7.41	504.58	7.43	226.11	51.86	-	-				
CO ₂	275.54	9.42	-	-	199.69	34.35	196.31	35.46				
Ar	132.56	12.04	132.63	11.99	122.70	18.58	124.43	17.43				

Table 3. Values of calculate bulk critical temperatures from Eq. (23) based on different literature reports of Kihara and L-J parameters for some fluids.

$$\frac{2\pi}{3} \left(\sigma^3 - (2a_k)^3 \right) = \frac{1}{8} \times \frac{kT_c}{P_C}$$
(35)

where T_c and P_c are in K and Pa, respectively.

Adjustment for Lennard–Jones potential function. For a two-parameter potential like Lennard–Jones, Eqs. (34 and 35) suffice and must be solved to compute σ_{LJ} and $(\varepsilon_k)_{LJ}$. Table 4 lists the values of adjusted L–J parameters for nitrogen, carbon dioxide, and a wide range of common hydrocarbons used in the literature. Equations 36 and 37 declare that T_c^* and P_c^* are constant for all components in Table 4 providing we substitute the values.

$$\left(1/T_c^*\right)_{LI} = 0.96275\tag{36}$$

Component	σ_{LJ} [Å]	$(\varepsilon_k)_{LJ}[K]$
N_2	3.128	121.40
CO ₂	3.238	292.86
CH_4	3.244	183.46
C_2H_6	3.724	293.95
C_3H_8	4.155	356.06
C_4H_{10}	4.519	409.29
C5H12	4.861	452.21
$C_{6}H_{14}$	5.171	488.70
C ₇ H ₁₆	5.456	520.08
$C_8 H_{18}$	5.731	547.52
C ₉ H ₂₀	5.980	572.17
C10H22	6.225	594.69
C11H24	6.465	615.20
C12H26	6.679	633.49

Table 4. Adjusted L-J parameters of nitrogen, carbon dioxide, and light to semi-heavy normal alkanes.

$$\left(1/P_{c}^{*}\right)_{LI} = 16.1313\tag{37}$$

On the other hand, v_c^* was constant in the first place ($v_c^* = 3b^*$) and is equal to 2π for L–J fluids. Accordingly, we have,

$$Z_c = \frac{v_c^* P_c^*}{T_c^*} = \frac{2\pi \times 0.96275}{16.1313} = \frac{3}{8}$$
(38)

which strongly supports the calculations of parameters and the hypotheses behind the approach. With this format, the macroscopic and microscopic theories of corresponding states are neatly related to each other, aligned with the literature established correlations²⁰.

Adjustment for Kihara potential function. A three-parameter potential function such as Kihara, however, requires another relation (for a_k). This third equation will be the definition of the reduced Kihara size parameter as follows:

$$a_k^* = \frac{2a_k}{\sigma_k} \tag{39}$$

Although Kihara parameters have different values regarding the property they have been fitted with, the ratio of the two size parameters a_k and σ_k as a_k^* appears to be almost **constant** 42. Thus, we need the value of a_k^* as the final step. In this study, we will exclusively obtain a_k^* through fitting the Kihara parameters with the DIPPR reports of B(T), using Eq. (10). Values of a_k^* determined in this work are brought in Table 5, and Eq. (40) can be used for n-alkanes with R² of 0.98. Complete details are presented in Supporting Information 1 and 2.

$$a_k^* = 0.219(\omega \times MW)^{0.3013} \tag{40}$$

With a_k^* in hand, we can use the adjustment method (Eqs. 34, 35, and 39) to calculate the adjusted Kihara parameters by which the critical conditions of a bulk fluid will be met. Their values are listed for different substances in Table 6, and Eqs. (41 and 42) are the fitted relations for ε_k and σ_k with R² of 0.990 and 0.999, respectively.

$$\left(\frac{1}{T_c^*}\right)_{Kihara} = 1.69024a_k^* + 0.925 \tag{41}$$

Component	N ₂	CO ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C4H10	C ₅ H ₁₂
$a_k^* = 2a_k/\sigma_k$	0.1666	0.4837	0.1456	0.2389	0.3678	0.4872	0.5718
Component	C ₆ H ₁₄	C7H16	C8H18	C ₉ H ₂₀	$C_{10}H_{22}$	$C_{11}H_{24}$	$C_{12}H_{26}$
$a_k^* = 2a_k/\sigma_k$	0.6000	0.6980	0.6678	0.7389	0.7772	0.8147	0.8767

Table 5. Value of a_k^* obtained from the second virial coefficient data fitting.

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Component	<i>a</i> _k [Å]	σ_k [Å]	$\varepsilon_k[K]$
N ₂	0.2610	3.1332	150.16
CO ₂	0.8152	3.3705	523.47
CH ₄	0.2364	3.2475	220.96
C ₂ H ₆	0.4469	3.7409	397.73
C_3H_8	0.7772	4.2264	560.99
$C_4 H_{10}$	1.1468	4.7079	734.18
C5H12	1.4889	5.2079	882.85
$C_{6}H_{14}$	1.6823	5.6079	980.08
$C_{7}H_{16}$	2.1871	6.2671	1139.2
C_8H_{18}	2.1529	6.4475	1168.2
C ₉ H ₂₀	2.6244	7.1036	1297.4
C10H22	2.9881	7.6895	1391.1
C111H24	3.4135	8.3795	1482.1
C12H26	4.2524	9.7014	1598.5

Table 6. Adjusted Kihara parameters of nitrogen, carbon dioxide, and light to semi-heavy normal alkanes.

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$$\left(\frac{1}{P_c^*}\right)_{kihara} = -25.095a_k^{*4} - 32.278a_k^{*3} + 22.037a_k^{*2} + 19.008a_k^* + 16.248$$
(42)

Even though T_c^* and P_c^* are component-dependent in the Kihara model, the critical molar volume has the same behavior $-v_c^* = 2\pi \left(1 - a_k^{*3}\right)$ – to reflect the fact that Z_c is constant (and equal to 3/8) for all vdW fluids regardless of the potential function. This can be simply checked through assuming an arbitrary value for a_k^* and calculating Z_c , as we did for L–J in Eq. (38).

As we perceived, T_c^* and P_c^* was constant for all matters following the L–J model. Since the Kihara potential somehow encompasses the L–J function in its formula, the intercepts of Eqs. (41 and 42) are expected to be equal to their corresponding values in Eqs. (36 and 37). Although they are not exactly the same, they are sufficiently close and the deviation can be attributed to the uncertainties in data employed for T_c and P_c^{-41} , fitting issues, or imperfect root finding. Thus, the corresponding states principle of Kihara fluids is indeed the generalized form of that of the Lennard–Jones model.

Variable energy parameter (\epsilon). Thus far, (1) the exact solution of the free energy integral was presented using the Kihara potential function and the critical temperature shift equation was derived (Section "How to better model the critical temperature of confined fluids?"), (2) a new thermodynamic-based adjustment method was employed, (3) the Kihara parameters were fitted using the DIPPR database of B(T), and (4) the adjusted Kihara and L–J parameters were listed for nitrogen, carbon dioxide, and normal alkanes from C1 to C12 (Section "Adjustment: the bulk critical conditions must be met in ").

The adjustment satisfied the critical point requirements of macroscopic fluids, but it does not necessarily enable the model to provide better predictions of pore critical temperature (T_{cp}) . As shown for CO₂ and C₂H₆ in Fig. 9, for both Kihara and L–J potentials, T_{cp} values predicted by the adjustment method deviate noticeably from the experimental values 4. This implicitly implies that the confinement effect is witnessed in larger pore sizes in



Figure 9. Comparison among the T_{cp} values from experimental reports 4 as well as the predictions of adjusted Kihara and adjusted L-J methods for (a) carbon dioxide and (b) ethane.

the Lennard–Jones model, sooner than that of the Kihara, and both earlier than the empirical observations. Such imperfection in the calculations, however, is happening while the free energy integral is solved exactly (making the EOS entirely exclusive for each component) and the adjustment is implemented to fulfill the bulk conditions. Therefore, the theory needs a moderator to alleviate the pore-scale problem.

Let us tackle the issue from a new and different perspective. The critical point is known as the characteristic state, where the liquid and gaseous phases of a substance become identical. At this point, the critical temperature is a measure of kinetic energy, therefore a relation between ε_k and T_c is quite expectable and reasonable²⁰:

$$\frac{\varepsilon}{k} = \varepsilon_k = A_1 T_c \tag{43}$$

where A_1 is a universal constant obtained by quantum mechanics studies. It is experimentally proved and measured for simple fluids (with spherical molecules) obeying the L–J potential function that A_1 is approximately equal to 0.77⁴⁴. Please refer to Supporting Information – Molecular Theory of Corresponding States for more explanations.

From the foregoing explanations, knowing that T_c and ε_k are of one type, and based on the shift of critical temperature of confined fluids, we can **infer** that the energy parameter of the potential function would accordingly shift. In other words, as a component has different critical temperature values at different pore radii, there might be also a possibility for ε_k to vary in pore size–which is designated herein as ε_{kp} . In fact, since tuning has always been prevalent among PVT researchers to accomplish their desired outcomes, we are considering ε_k a **tuning parameter** that decreases as pore size shrinks.

So why manipulating ε_k rather than σ_k or a_k ? Along the lines of ε_k and T_c , there is a relation between the size parameters a_k or σ_k and the critical molar volume (v_c) , because the latter represents the molecular size. The point is, however, that v_c of a bulk fluid does not really differ from the confined one. Not only this claim is theoretically conspicuous from Eq. (25) where there is no confinement term (no sign of A), but experiments have also made the same assertion as well⁴³. Even if there were any shift of v_c regarding pore shrinking, it would be irrelevant to choose a distance parameter for calibrating an energy parameter (T_c). Thus, ε_k (or in fact ε) seems to be the only choice for manipulation. Meanwhile, a_k and σ_k must be involved in the calculations as they have been determined from the adjustment process.

To be more specific, such an inference can be conceptually paraphrased as if the parameter ε_k in the original integral (Eq. 7) is a function of the pore area (A) over which the integration is taken, i.e., Eq. (44). However, the solution to the integral, written as Eq. (45), does not fundamentally differ from the original solution (Eq. 8), except ε_k must be replaced by ε_{kp} .

$$\frac{1}{V} \int_{A} \left(1 - exp \left[-\frac{4}{T} \varepsilon_k[A] \left(\left(\frac{\sigma_k - 2a_k}{r - 2a_k} \right)^{12} - \left(\frac{\sigma_k - 2a_k}{r - 2a_k} \right)^6 \right) \right] \right) dr$$
(44)

$$I(A, a_k^*, T/\varepsilon_k[A]) = C_0(a_k^*, T/\varepsilon_k[A]) + \frac{C_1(a_k^*, T/\varepsilon_k[A])}{\sqrt{A}} + \frac{C_2(a_k^*, T/\varepsilon_k[A])}{A}$$
(45)

We deliberately write $\varepsilon_k[A]$ instead of $\varepsilon_k[r_p]$ to avoid ambiguity. Indeed, r (intermolecular distance) is totally different from r_p which is the maximum distance that two molecules can be placed far from each other, and almost equates the pore diameter ($r_{max} \cong 2r_p$). Substituting $\varepsilon_k[A]$ for ε_k , we still should refer to Eq. (23) to calculate the pore critical temperature, because, the variable energy parameter has no effect on the procedure with which Eq. (23) is obtained, nor on the dimensionless diagrams.

How to determine the value of ε_{kp} ? Presume that universally unique and reliable experimental measurements of critical temperature of confined pure fluids are available. In other words, the present (r_p, T_{cp}) data points are real, certain, and precise. In this case, the corresponding ε_{kp} will be obtained if we substitute the known properties of the component $(\sigma_k, a_k^*, r_p, T_{cp})$ into Eq. (23). With a reverse rooting find try, ε_{kp} will be accurately determined as the unknown of the equation. Nonetheless, literature reports of T_{cp} , whether empirically measured or numerically simulated, are highly uncertain and scattered. Therefore, we resort to calculating ε_{kp} for each available pair of (r_p, T_{cp}) from any reference, and will propose a model that fits best, if possible. We state "if possible", because on occasion, the model is not able to give an ε_{kp} less than the bulk ε_k (ε_{kb}) for some matters such as CO₂, or there is too small number of data points to fit a model, like C₃H₈.

Similar to the fact that T_{cp} equates T_c when r_p increases and approaches infinity, ε_{kp} must behave the same towards ε_{kb} (i.e. ε_k from adjustment). Thus, the fitting model would possess a format as below,

$$\varepsilon_{kp} = \varepsilon_{kb} \left(1 - \frac{\alpha}{A^{\beta}} \right) \tag{46}$$

where $A = \pi \left(\left(r_p - \delta_p \right) / \sigma_k \right)^2$, α and β are component-dependent fitting constants.

Figure 10 summarizes the notion of pore-size-dependent energy parameter and depicts how the potential curve changes as a result. Although changing ε_k appears to be merely a tuning attitude that we have adopted, we deeply look forward to knowing whether the confinement phenomenon truly affects the ultimate and real intermolecular interactions. Yet, molecular-scale experimental measurements are extremely challenging to perform and are accompanied by uncertainties.



Figure 10. Depiction of pore-dependent energy parameter.

Results and discussion

Calculating the values of ε_{kp} (**Training Section**). For the very first time, we have gathered 76 data points of pore critical temperature reported in the literature, the largest collection ever employed. This collection covers 9 components including methane, ethane, propane, n-butane, n-pentane, n-octane, n-decane, nitrogen, and carbon dioxide, from 13 different references overall^{1-4,9,11,13-17}. Values of ε_{kp} (Kihara) are calculated and categorized with respect to components and references, and are listed in Table 7. This classification helps readers to conveniently select their desired ε_{kp} based on their and the reference's hypotheses.

Methane and ethane had the greatest number of available T_{cp} reports for training, i.e. 19, though the scattering of ethane points is much more than that of methane, which is readily notable from their R². As discussed earlier, the obtained ε_{kp} from our theory had a greater value than ε_{kb} for a few numbers of (r_p, T_{cp}) points. On the one hand, this is because the points would need a flexibility beyond what the model is capable of. On the other hand, there is always an amount of uncertainty in both numerical simulations and empirical measurements to which such an imperfection could be assigned. That is why it was impossible to fit a model for CO₂ whose two ε_{kp} values out of the three, were bigger than its bulk ε_k .

Equations (47 and 48) can be respectively used for the values of α and β of Table 7, with R² of 0.99 and 0.96.

$$\alpha = (-50.8878 + 459.659 \times a_k^*) / (-15.8293 + MW + \omega^2)$$
(47)

$$\beta = 1.76384 - 2.11073/\sqrt{\alpha} + 0.74907/\alpha \tag{48}$$

The Lennard–Jones potential function is not an appropriate choice of changing ε_{kp} . Although it is feasible to determine $(\varepsilon_{kp})_{LJ}$ for each (r_p,T_{cp}) point, the insufficient flexibility of this potential forbids having valid values; for the Kihara model, only 12 data points (16% out of 76) had an ε_{kp} greater than ε_{kb} . In opposite, L-J suffers more from this problem for which there were 37 (almost 50%) theoretically-false results (See Supporting Information. xlsx). It is directly related to the curvature of $U(r_{12})$ and the fact that mostly the predictions provided by the L–J model are underestimated. Therefore, the Kihara potential function is, again, a more decent choice to go for.

Solid verification of the proposed model (testing section). In this section, we assess the performance of our model with another 18 data points of recently published critical shift reports. These would include measured T_{cp} and P_{cp} values of methane⁴⁶, and Tcp reports of carbon dioxide and normal heptane⁴⁷, all within the range of 3–20 nm. Not only they include light and heavy components, but they also represent both hydrocarbon and non-hydrocarbon families of commonly investigated fluids, especially CO₂. These 18 points are regarded as the test points of our work, constituting 20% of the whole 94 evaluated data points.

Two critical shift models presented by Zhang et al.²³ (Eq. 49) and Yang et al.³¹ (Eq. 50) are employed herein for comparison. Both models incorporate the effect of adsorption thickness and are developed for the Lennard–Jones fluids.

$$\frac{T_c - T_{cp}}{T_c} = \frac{P_c - P_{cp}}{P_c} = 0.7197 \left(\frac{\sigma_{LJ}}{r_p - \delta_p}\right) - 0.0758 \left(\frac{\sigma_{LJ}}{r_p - \delta_p}\right)^2 \tag{49}$$

$$\frac{T_c - T_{cp}}{T_c} = \frac{P_c - P_{cp}}{P_c} = 3.374 \times \left(\frac{r_p - \delta_p}{\sigma_{LJ}}\right)^{-1.637}$$
(50)

As plotted in Fig. 11, the model developed in this study with its pore-size-dependent energy parameter has performed much better than other models in predicting the effect of confinement on fluids critical properties. This was more outstanding for critical pressure in particular, because no training data of P_{cp} has been included

	CH4			C_2H_6			C ₄ H ₁₀ C ₃ H ₁₂			C ₈ H ₁₈			C10H22			N ₂			CO ₂					
Ref	<i>r</i> _p	T _{cp}	ε_{kp}	<i>r</i> _p	T _{cp}	ε_{kp}	<i>r</i> _p	T _{cp}	ε_{kp}	<i>r</i> _p	T _{cp}	ε_{kp}	<i>r</i> _p	T _{cp}	ε_{kp}	r _p	T _{cp}	ε_{kp}	<i>r</i> _p	T _{cp}	ε_{kp}	<i>r</i> _p	T _{cp}	ε_{kp}
	nm	к	К	nm	к	к	nm	к	к	nm	к	К	nm	К	к	nm	к	К	nm	К	К	nm	К	К
4				4.57	297.5	406.3																4.57	294.5	522.5
				6.08	304.1	410.5																6.08	301.3	530.6
				8.15	304.6	407.5																8.15	303.0	530.5
13																								
Mica	4.22	182.3	222.2				4.28	397.5	718.3				5.54	530.4	1116									
	3.21	176.6	218.6				3.26	382.7	701.5				4.41	516.0	1093									
	2.69	171.3	214.7				2.71	374.6	694.9				3.30	503.8	1079									
	2.15	164.7	210.4				2.17	359.3	678.3				2.20	466.9	1022									
	1.63	152.4	200.6				1.64	331.2	643.9				1.66	429.4	960.9									
13																								
Graphite	4.14	183.4	223.7				4.17	402.1	727.5				5.28	540.6	1139									
	3.15	177.9	220.5				3.19	389.8	715.4				4.25	531.7	1128									
	2.61	174.3	219.0				2.68	379.0	703.7				3.22	513.9	1101									
	2.11	169.0	216.3				2.15	361.6	683.4				2.17	470.7	1031									
	1.62	152.2	200.7				1.63	324.2	630.5				1.65	416.6	932.8									
17	2	155.2	199.8	2	248.7	360.7				2	337.3	693.7				2	475.9	749.1						
	3	172.7	214.8	3	273.7	383.1				3	375.7	749.9				3	542.4	928.6						
	5	179.8	217.5	5	282.4	384.1				5	396.4	772.4				5	575.6	1076						
				7	286.8	385.4				6	399.7	774.1												
1,2,3																			1.2	87	121.8			
																			1.9	98.12	129.5			
																			2.2	103	134.1			
																			3.0	105	133.5			
																			3.2	105	133.0			
																			3.9	112	140.3			
9	2	158.1	203.4																					
	3	175.8	218.5																					
	5	183.4	221.8																					
14	7	183.3	219.0	7	292	392.3																		
	10	186.0	220.3	10	296.3	394.4																		
15				3	258	361.1																		
				4	281.5	387.0																		
				5	292	397.2																		
				6	298	402.4																		
				7	300	403.1																		
				8	302	404.2																		
				9	304	405.6																C_3H_8		
16				5	285.1	387.7																rp	T _{cp}	ε_{kp}
				6	292.5	395.0																nm	К	К
11	2.03	169.7	218.0	2.03	269.5	390.2	2.03	372.0	706.8													2.03	320.7	538.4
α	74.963			5.8639			7.0572			0.8501			1.7739			1.5252			0.6989			Not Avail- able		
β	1.5236			0.9898			1.1075			0.2694			0.7408			0.3919			0.3443			Not Avail- able		
R ²	0.75				0.40		0.86			0.93			0.96			0.99			0.87			Not Avail- able		

Table 7. Calculated values of ε_{kp} for each component based on different sources of T_{cp} reports along with their fitting coefficients.

during model development in the previous section. The average deviation of our model was just below 2%, whereas the models of Zhang 2019 and Yang 2019 had the average errors of 4.4% and 4.5%, respectively.

Phase diagrams and discussion on capillary condensation occurrence. Pressure–Volume isotherm diagrams of the van der Waals and Peng-Robinson (PR)⁴⁸ EOSs were evaluated in the literature where they were associated with the Lennard–Jones potential function (LJ-vdW and LJ-PR). In spite of the LJ+vdW⁶, as it is controversially reported by Islam et al.³³, the P–V axial isotherms of LJ+PR do not show capillary condensation at a same reduced temperature ($T_r = T/T_c$) and the confined fluid's phase appears to be constantly supercritical. To scrutinize this issue for the Kihara potential function, we will first draw a comparison between the PV isotherm diagrams of Kihara+vdW and Kihara+PR models at different T_r values. Then, the effect of potential type and employing pore-size-dependent ε_k on maxwell construction will be investigated.

P-V isotherms diagrams of Peng-Robinson vs. van der Waals. In order to incorporate the critical shift phenomena into EOS calculations, we replace the T_c and P_c parameters in the attractive (*a*) and repulsive (*b*) terms of



Figure 11. Cross plots of critical shift estimations from this study along with two other models in the literature 23,31 for (**a**, **b**) methane 46, (**c**) carbon dioxide, and (**d**) normal heptane 47.

EOSs with the shifted version derived from this study (T_{cp} , P_{cp}). In this section, the ε_{kp} concept is employed and its value is computed by Eq. (46), using the α and β presented in Table 7.

We slightly reduce the temperature from the critical point region for methane, as an example. Figure 12 shows how the confinement influences the isotherm curves and the prediction of fluid's state. Both vdW and PR equations of state perfectly expose the presence of Maxwell construction for the bulk fluid (black dashed line), and also the tendency of its confined case at $r_p = 5nm$ (purple dashed line) to act the same. However, the critical temperature at $r_p = 2nm$ is less than that of the current system, therefore the fluid must be homogenous but supercritical. This is well supported by the solid green and orange lines for the axial and transverse pressures, respectively, where $P_{zz} < P_{xx}$. It is well worthy to mention that the vdW EOS generates a smaller two-phase region, or in fact, less v_g . Consequently, isotherm lines of this EOS are more inclined towards showing capillary condensation sooner than their correspondents of PR.

Decreasing the temperature and maintaining the transverse A constant, we observe a loop appearing for the axial pressure P_{zz} when T is less than T_{cp} at 2 nm (Fig. 13). If we take the temperature even lower, the transverse pressure P_{xx} also commences to presents a loop as well as the axial part (Fig. 14), which indicates both Kihara + vdW and Kihara + PR models reveal capillary condensation in the axial part at the same reduced temperature. A Video file is provided as supplementary material (which completely embeds the motion of P–V isotherms of Kihara-PR for methane through Figs. 12, 13, 14), so that the occurrence of capillary condensation of both bulk and confined fluids will be readily understandable.

The effect of $U(r_{12})$ and ε_{kp} . The effect of potential function type and its variable energy parameter on Maxwell construction in P–V diagram is thoroughly explored in Supporting Information 3. Overall, it is interesting that the isotherm curves of Peng-Robinson equation of state when coupled with the Lennard–Jones potential func-



Figure 12. Volume dependence of the axial and transverse pressure tensor components of methane at $T_r = 0.94$ for different r_p values obtained from (**a**) Peng-Robinson and (**b**) van der Waals equations of state associated with the Kihara potential function.



Figure 13. Capillary condensation of axial pressure for methane at $T_r = 0.82$ obtained from (**a**) Peng-Robinson and (**b**) van der Waals equations of state associated with the Kihara potential function. Dashed line evidence the Maxwell construction for two-phase equilibrium.

tion, perfectly shows capillary condensation for both axial and transverse components of the pressure tensor when the temperature is decreased. This is properly in contrast to what has been reported and explained in the literature by Islam et al.³³. Moreover, at each T_r , the Kihara-PR model with ε_{kb} results in widest two-phase regions compared to those of the Lennard–Jones since the use of constant energy parameter leads to greater T_{cp} predictions. By applying ε_{kp} , the diagrams seem more rational and reliable in terms of the involved T_{cp} , and of course, they do not readily fail in the demonstration of capillary condensation unless at relatively low temperatures.

Model validation (Application in mixtures equilibrium). After we gained a better understanding of intermolecular forces and fluids' molecular behavior by the proposed model, the best practice to predict and interpret the properties of mixtures would be applying the thermodynamic methods to phase equilibrium problems 20. In this section the validation of the proposed theory will be examined. Zhang et al.³⁴ have modified the Peng-Robinson equation of state through involving the L-J critical shift model⁶, and employed their model to



Figure 14. Capillary condensation of axial pressure and the tendency of the transverse pressure to construct the two-phase region for methane at $T_r = 0.80$ obtained from (**a**) Peng-Robinson and (**b**) van der Waals equations of state associated with the Kihara potential function. Dashed line evidence the Maxwell construction for two-phase equilibrium.

predict the equilibrium properties of a confined ternary system comprising i-C4, n-C4, and n-C₈ in micro/nano-scale channels of $10\mu m$ and $100 nm^{49}$.

Similarly, we implement the flash calculations on this system using the analytical model we have derived for the critical shift along with the proposed approach of pore-size-dependent energy parameter.

The details of the vapor–liquid equilibrium (VLE) calculations we have utilized in our approach are presented in Supporting Information 3. The results are listed and compared to the experimental reports⁴⁹ and the results of Zhang et al., in Table 8³⁴. As the table presents, our calculations are more agreeable with the true values, and our model have reduced the error of Lennard–Jones model by more than 6%.

Summary and conclusion

Critical shift and phase transition of confined fluids have continually been a focal point of interest in a multitude of studies conducted with the help of molecular thermodynamics science. Yet, the lack of a better and more precise fundamental approach has always been noticed.

Overall, the following points can be concluded from the breakthroughs achieved in the fundamentals from this study:

- In spite of the Lennard–Jones (L–J) model, the energy integral should be calculated exclusively for each fluid when using the Kihara potential function, thereby leading to more accurate predictions. In this regard, each component has its specific integration constants (C₀, C₁, and C₂), whereas the study for L–J proposes one unique set of constants for all fluids.
- The exact analytical solution to the second virial coefficient formula of Kihara fluids is presented for the very first time and the Kihara parameters are determined based on B(T) data fitting with which the value of reduced Kihara parameter is obtained.
- The model must be able to render the bulk fluid's critical properties when the pore radius approaches infinity, whereas it is not. The treatment of addressing this issue is called 'Adjustment'. In the previous work of L-J, the adjustment was merely a correlation-based enhancement and lacked a thermodynamic basis. In our model, however, the values of Kihara parameters are determined in a way that the critical shift equation leads to the bulk critical properties of matters.
- In comparison to the experimental measurements, the exact solution of both models (Kihara and L-J) does not lead to acceptable predictions of T_{cp} . Hence, a novel idea is proposed and justified in which the energy parameter of Kihara fluids (ε_k) varies with respect to pore size reduction (ε_{kp}) and equated the bulk state (ε_{kb}) at $r_p \rightarrow \infty$.

Finally, the proposed idea is supported by a collection of 94 critical shift data points and its performance is validated by evaluating the VLE properties of a ternary mixture, where our error was almost half of the L-J's.

The followings are the advantages, disadvantages/limitations of this work along with suggestions for probable future works:

Parameters	Before flash ⁴⁹			After flash ⁴⁹			After flash (L-J) ³⁴				After flash (Kihara) – This study			
1- Constant pressure case														
Temperature (°C)	24.9			71.9										
Pressure (Pa)	85,260									AARD (%)				AARD (%)
Liquid (iC4, nC4, C8) mol %	15.47	4.53	80	4.88	1.87	93.25	5.09	1.68	93.23	4.83	4.8333	1.8484	93.320	0.728
Vapor (iC4, nC4, C8) mol %	0	0	0	64.35	16.82	18.83	62.84	17.56	19.6	3.61	64.072	16.783	19.146	0.778
Liquid fraction (mol %)	100			82.2			82.03			0.21	82.044			0.190
Vapor fraction (mol %)	0			17.8			17.97			0.96	17.956			0.875
IFT (mJ/m^2)				16.24			15.68			3.45	14.890			8.313
P _{cap} micro-channel (kPa)				3.38			1.92			43.20	2.579			23.70
P _{cap} nano-channel (kPa)				286.91			185.63			35.30	231.12			19.44
Average %										13.08				7.72
2- Constant temperature case														
Temperature (°C)	71.9													
Pressure (Pa)	839,925			426,300										
Liquid (iC4, nC4, C8) mol %	61.89	18.11	20	28.59	11.15	60.26	18.98	6.44	74.58	33.21	28.598	11.149	60.254	0.017
Vapor (iC4, nC4, C8) mol %	0	0	0	75.82	21.01	3.16	76.66	19.35	3.99	11.76	75.798	21.018	3.1833	0.269
Liquid fraction (mol %)	100			29.5			30.38			2.98	29.467			0.113
Vapor fraction (mol %)	0			70.5			69.62			1.25	70.533			0.047
IFT (mJ/m^2)				13.33			12.89			3.30	12.217			8.51
P _{cap} micro-channel (kPa)				2.77			1.88			32.13	2.116			23.61
P _{cap} nano-channel (kPa)				235.54			182.49			22.52	183.13			22.25
Average %										15.31				7.81

Table 8. Experimental VLE properties of a ternary system <u>49</u> compared to the reported calculations of L-J model <u>34</u> and this model proposed in this study for 1-Constant Pressure Case and 2- Constant Temperature Case in 10 μ m and 100 nm channels.

- Advantages The critical shift modeling is done exactly without any simplifying assumptions or approximations. This work benefits from a better adjustment method than the previous works of L-J. The notion of pore-size-dependent energy parameter is presented for the very first time that enables researchers to achieve the most precise predictions of confined fluid's behavior providing enough experimental values are available. Employing the Kihara potential function gives more accurate results and better flexibility rather than the Lennard–Jones.
- *Disadvantages/Limitations* The pore critical temperature cannot be directly calculated since its formula is a little complex, and a root finding process should be followed. However, a precalculated type-curve was presented for convenience and ease of use. For similar works, sufficient number of experimental data points will be needed to calibrate the energy parameter of potential function.
- Suggestions for future works It is recommended to calibrate the energy parameter with pore critical pressure data, providing sufficient number of data points are accessible, to determine whether the results are far from those calibrated by pore critical temperature in this work.

Data availability

The data of this study will be available upon request via contacting the corresponding author (m.khorsand@ aut.ac.ir).

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Competing interests

The authors declare no competing interests.

Additional information

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