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An EQT-based cDFT approach for a confined Lennard-Jones fluid mixture

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Empirical potential-based quasi-continuum theory (EQT) provides a route to incorporate atomistic detail into continuum framework such as the Nernst-Planck equation. EQT can also be used to construct a grand potential functional for classical density functional theory (cDFT). The combination of EQT and cDFT provides a simple and fast approach to predict the inhomogeneous density, potential profiles, and thermodynamic properties of confined fluids. We extend the EQT-cDFT approach to confined fluid mixtures and demonstrate it by simulating a mixture of methane and hydrogen inside slit-like channels of graphene. We show that the EQT-cDFT predictions for the structure of the confined fluid mixture compare well with the molecular dynamics simulation results. In addition, our results show that graphene slit nanopores exhibit a selective adsorption of methane over hydrogen. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4930924]

I. INTRODUCTION

Fluids and their mixtures in confined geometries ranging from nano- to micro-sized dimensions behave quite different than those in bulk.^{1,2} These are interesting systems to study because of their appealing applications, such as adsorption, wetting, lubrication,³ drug delivery,⁴ separations, and geophysical applications.⁵ A key characteristic of confined fluids is the inhomogeneity, imposed by the wall-fluid interactions and confinement. The layering of fluid molecules near a wall has profound effects on the properties of confined fluids. For instance, the velocity profile of a nanoconfined fluid between two surfaces is strongly influenced by the density oscillations.^{6,7} Hence, an accurate and thorough understanding of this inhomogeneous behavior is central for many applications in the field of nanotechnology.

Over the past few decades, atomistic descriptions such as molecular dynamics (MD) and Monte Carlo (MC) simulations have been widely used to study fluids and their mixtures in nanoconfinement.^{5,8} However, it is computationally expensive to do full molecular simulations for systems involving multiple length and time scales ranging from the quantum to atomic to continuum scales. On the other hand, it has been shown that to study fluid-fluid or fluid-solid interfaces, classical continuum descriptions fail to accurately capture atomistic details.^{9,10} Thus, there is a need for a multiscale approach that is not only as fast as classical continuum methods but also as accurate as atomistic simulations. In addition, the method should be computationally simple, especially when dealing with multicomponent fluids.

An empirical potential-based quasi-continuum theory (EQT) is a multiscale approach that provides a framework to seamlessly integrate atomistic details into a continuum-based model. Over the past few years, EQT has been developed and studied to predict structure of single component Lennard-Jones (LJ) fluids,^{11,12} carbon dioxide,¹³ and water^{14,15} in nano

slit-like channels. In these studies, for a slit-channel system, with z as the normal direction to the walls, the 1-D steady-state Nernst-Planck (NP) equation,

$$\frac{d}{dz}\left(\frac{d\rho}{dz} + \frac{\rho}{RT}\frac{dU}{dz}\right) = 0,$$
(1)

with boundary conditions

$$\rho(0) = \rho(L) = 0,$$
(2a)

$$\frac{1}{L} \int_0^L \rho(z) \, dz = \rho_{avg},\tag{2b}$$

is solved self-consistently to obtain the density and potential distribution of a confined fluid. In Eqs. (1) and (2), ρ is the fluid density, U is the total potential, T is the fluid temperature, R is the ideal gas constant, L is the channel width, and ρ_{avg} is the average density of the confined fluid. The main idea of EQT is to incorporate atomistic details into U by using empirical pair potentials, continuum representation of the wall and fluid atoms, and an approximation for the pair correlations in the fluid medium.

EQT potentials can also be used to construct the excess free energy functional $(F^{\text{ex}}[\rho(\mathbf{r})])$ required in the classical density functional theory (cDFT). In cDFT, the key variable is the single particle density, $\rho(\mathbf{r})$. It is based on the theorem that the free energy of an inhomogeneous fluid is a unique functional of $\rho(\mathbf{r})$, independent of any external potential.^{16–18} The main effort is thus to find an approximate functional for Helmholtz free energy based on density distributions. Many applications of cDFT are based on the mean-field theory (MFT),¹⁹⁻²² in which the structural correlations in the excess free energy are neglected. However, there are both quantitative and even qualitative discrepancies reported between MFT and molecular simulation results.^{23,24} There are also methods based on the modified MFT,²⁵ weighted-density approximation (WDA),^{26–28} and perturbative methods,^{24,29–31} where the excess free energy functional is Taylor expanded around a homogeneous reference system, and an approach

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based on the coarse-grained lattice gas model,³² which has recently been used to study the adsorption and desorption of argon molecules inside a nanopore.

In recent work, we developed an EQT-based expression for the excess Helmholtz free energy functional in cDFT for confined single component Lennard-Jones fluids.³³ We demonstrated that the combination of EQT and cDFT (EQTcDFT) provides a simple and fast approach that not only predicts the equilibrium structure but also other thermodynamic properties, such as the local pressure profile, adsorption, solvation force, and surface tension.

In this study, we extend the EQT-cDFT approach for confined fluid mixtures and employ it to obtain equilibrium density distributions of the methane and hydrogen mixtures in slit-like graphene channels of various widths. Unlike the Nernst-Planck approach (Eq. (1)), EQT-cDFT approach eliminates the requirement for *a priori* knowledge of the average density, ρ_{avg} , for each channel. Instead, ρ_{avg} can be obtained as an output of this method for various channel widths.

The remainder of the paper is organized as follows. In Sec. II, a general formalism of the EQT-cDFT approach is described. In Sec. III, essential details on MD simulations are provided. In Sec. IV, theoretical predictions by EQT-cDFT are compared to molecular dynamics simulations of a supercritical binary mixture of methane and hydrogen molecules inside a slit-like graphene channel. Finally, conclusions are provided in Sec. V.

II. THEORY

In this work, we consider a multicomponent mixture of fluids confined inside a slit-like channel. For such a system, the total potential of a fluid component α , $U_{\alpha}(\mathbf{r})$, at a given location \mathbf{r} can be computed as a sum of wall-fluid and fluid-fluid interactions,

$$U_{\alpha}(\mathbf{r}) = U_{\alpha}^{\text{wf}}(\mathbf{r}) + U_{\alpha}^{\text{ff}}(\mathbf{r}), \qquad (3)$$

where $\alpha = 1, 2, ..., m$ is the label of a fluid component, *m* is the number of fluid components in the mixture, U_{α}^{wf} and U_{α}^{ff} are the wall-fluid and fluid-fluid potentials of component α , respectively.

In the continuum approximation, the wall structure is locally represented by a single density distribution, $\rho_w(\mathbf{r})$. Therefore, the wall-fluid potential can be written as

$$U_{\alpha}^{\rm wf}(\boldsymbol{r}) = \int \rho_{\rm w}(\boldsymbol{r}') \, u_{\alpha}^{\rm wf}(|\boldsymbol{r}-\boldsymbol{r}'|) d\boldsymbol{r}', \qquad (4)$$

where u_{α}^{wf} is the wall-fluid pair potential for component α .

In contrast with the wall-fluid potential, the fluid-fluid interactions are not trivial and require special considerations due to fluid-fluid correlations. For a mixture of fluids, the fluid-fluid potential energy can be expressed in terms of the two-body correlation, $g^{(2)}(\mathbf{r},\mathbf{r}')$, and the pair potential between different components as

$$U_{\alpha}^{\rm ff}(\boldsymbol{r}) = \sum_{\beta=1}^{m} \int \rho_{\beta}(\boldsymbol{r}') g_{\alpha\beta}^{(2)}(\boldsymbol{r},\boldsymbol{r}') u_{\alpha\beta}^{\rm ff}(|\boldsymbol{r}-\boldsymbol{r}'|) d\boldsymbol{r}', \quad (5)$$

where $u_{\alpha\beta}^{\rm ff}$ is the fluid-fluid pair potential between components α and β . There exist several approximations for the twobody correlation. Among them, MFT has been widely used, especially in the cDFT literature to treat long-range attractions in the excess part of the intrinsic Helmholtz free energy.^{19–22} Although MFT is computationally convenient and easy to grasp, it can be quantitatively problematic and even sometimes qualitatively incorrect.^{23,24,30} In addition, since the pair potential in Eq. (5) is highly repulsive as $r \rightarrow 0$, the mean field approximation will cause numerical singularities. To avoid this problem and to introduce a better approximation for the pair correlation, we follow an approach similar to the work of Tang and Wu.³⁰ We approximate the two-body correlation by

$$g^{(2)}(\boldsymbol{r},\boldsymbol{r}') \approx g^{\rm hs}\left(|\boldsymbol{r}-\boldsymbol{r}'|\right),\tag{6}$$

where g^{hs} is the radial distribution function (RDF) of homogeneous hard spheres at bulk density, ρ_b . To fully determine the hard sphere radial distribution function, we need to know the packing fraction $\eta = \pi \rho_b d^3/6$, where *d* is the hard sphere diameter. The hard sphere diameter for each component is calculated based on the relation proposed by Barker and Henderson,³⁴

$$d(T) = \int_0^\sigma \left(1 - \exp\left[-\frac{u^{\rm ff}(r)}{k_B T}\right]\right) dr,\tag{7}$$

where σ is the length-scale parameter for LJ interaction and $k_{\rm B}$ is the Boltzmann constant. The RDFs are obtained using existing analytical expressions for additive hard sphere mixtures based on Percus-Yevick approximation.^{35,36} A complete review on different closures and approximations can be found elsewhere.³⁷

To account for errors due to the hard sphere RDF approximation, we introduce an isotropic correlation-correction potential denoted by u_{ccp}^{ff} . In EQT, the correlation-correction function is modeled using uniform cubic B-splines,

$$u_{\rm ccp}^{\rm ff}(r) = \begin{bmatrix} 1 & t & t^2 & t^3 \end{bmatrix} \frac{1}{6} \begin{bmatrix} 1 & 4 & 1 & 0 \\ -3 & 0 & 3 & 0 \\ 3 & -6 & 3 & 0 \\ -1 & 3 & -3 & 1 \end{bmatrix} \begin{bmatrix} c_j \\ c_{j+1} \\ c_{j+2} \\ c_{j+3} \end{bmatrix}, \quad (8)$$

where *r* is the separation distance between any two fluid molecules with the cut-off radius denoted by R_{cut} . The separation distance is discretized into n-1 intervals of equal size $\Delta r = R_{\text{cut}}/(n-1)$ such that $r_i = i \times \Delta r$, where $i \in (0, \ldots, n-1)$. In Eq. (8), the n+2 values $\{c_j\}$ are called spline knots where index j is determined such that $r_j \leq r \leq r_{j+1}$, and *t* is given by

$$t = \frac{r - r_j}{\Delta r}.$$
(9)

Therefore, using Eqs. (6) and (8), Eq. (5) can be simplified to

$$U_{\alpha}^{\rm ff}(\boldsymbol{r}) = \sum_{\beta=1}^{m} \int \rho_{\beta}(\boldsymbol{r}') \left(u_{\alpha\beta}^{\rm ff}(|\boldsymbol{r}-\boldsymbol{r}'|) g_{\alpha\beta}^{\rm hs}(|\boldsymbol{r}-\boldsymbol{r}'|) + u_{\rm ccp,\ \alpha\beta}^{\rm ff}(|\boldsymbol{r}-\boldsymbol{r}'|) \right) d\boldsymbol{r}'.$$
(10)

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As mentioned in Sec. I, EQT potentials can be employed in cDFT, i.e., in EQT-cDFT approach. cDFT is a theoretical tool to determine the properties of inhomogeneous fluids in equilibrium.^{17,18} For an open system that is in equilibrium with a bulk phase, the relevant thermodynamic potential is the grand potential Ω . In cDFT, for a multicomponent fluid system in the presence of an external potential V_{α}^{ext} , Ω is written as

$$\Omega[\{\rho_{\alpha}(\mathbf{r})\}] = F^{\mathrm{id}}[\{\rho_{\alpha}(\mathbf{r})\}] + F^{\mathrm{ex}}[\{\rho_{\alpha}(\mathbf{r})\}] + \sum_{\alpha=1}^{m} \int [V_{\alpha}^{\mathrm{ext}}(\mathbf{r}) - \mu_{\alpha}] \rho_{\alpha}(\mathbf{r}) d\mathbf{r}, \quad (11)$$

where μ_{α} is the chemical potential of the α th component. Here, F^{id} is the ideal part (ideal non-interacting system) of the intrinsic Helmholtz free energy for which the analytical expression is given by

$$F^{\text{id}}\left[\left\{\rho_{\alpha}\left(\boldsymbol{r}\right)\right\}\right] = k_{\text{B}}T\sum_{\alpha=1}^{m}\int\rho_{\alpha}\left(\boldsymbol{r}\right)\left(\ln\left[\rho_{\alpha}\left(\boldsymbol{r}\right)\Lambda_{\alpha}^{3}\right] - 1\right)d\boldsymbol{r},$$
(12)

where Λ_{α} represents de Broglie wavelength of component α . The challenging term in Eq. (11) is the excess free energy, F^{ex} , due to the fluid-fluid interaction. In the general case, the exact expression for this term is still unknown¹⁶ and there exist approximations based on the fundamental-measure theory (FMT),^{30,38–40} modified FMT (MFMT),^{41–43} first-order mean-spherical approximation (FMSA),⁴⁴ accurate empirical equation of state,²⁷ and statistical associating fluid theory (SAFT).^{45–48}

According to the variational principle,

$$\frac{\delta\Omega\left[\left\{\rho_{\alpha}\left(\boldsymbol{r}\right)\right\}\right]}{\delta\rho_{\alpha}}\bigg|_{\rm eq} = 0,\tag{13}$$

and therefore, the equilibrium density distribution satisfies

$$\rho_{\alpha}(\mathbf{r}) = \rho_{\alpha,b} \exp\left(-\frac{1}{k_B T} \left[V_{\alpha}^{\text{ext}}(\mathbf{r}) + \frac{\delta F^{\text{ex}}[\{\rho_{\alpha}(\mathbf{r})\}]}{\delta \rho_{\alpha}(\mathbf{r})} - \mu_{\alpha}^{\text{ex}}\right]\right), \quad (14)$$

where the bulk chemical potential μ_{α} has been decomposed into ideal (μ_{α}^{id}) and excess (μ_{α}^{ex}) parts, and the ideal part can be related to the density of the bulk phase for each component ($\rho_{\alpha,b}$). Using the expression for the fluid-fluid potential given in Eq. (10), we can construct the EQT excess free energy of the confined mixture as

$$F^{\text{ex,EQT}}[\{\rho_{\alpha}(\boldsymbol{r})\}] = \frac{1}{2} \sum_{\alpha=1}^{m} \int \rho_{\alpha}(\boldsymbol{r}) U_{\alpha}^{\text{ff}}(\boldsymbol{r}) d\boldsymbol{r}.$$
 (15)

In the bulk phase, the potential energy per particle for each component, $U_{\alpha,b}^{\text{ff}}$, can be written as follows:

$$U_{\alpha,b}^{\rm ff} = 4\pi \sum_{\beta=1}^{m} \rho_{\beta,b} \int r^2 \left(u_{\alpha\beta}^{\rm ff} \left(|\boldsymbol{r} - \boldsymbol{r}'| \right) g_{\alpha\beta}^{\rm hs} \left(|\boldsymbol{r} - \boldsymbol{r}'| \right) + u_{\rm ccp,\ \alpha\beta}^{\rm ff} \left(|\boldsymbol{r} - \boldsymbol{r}'| \right) \right) dr.$$
(16)

Similar to Eq. (15), we can construct the bulk excess free energy by using Eq. (16),

$$F_{b}^{\text{ex,EQT}}[\{\rho_{\alpha,b}\}] = \frac{1}{2} \sum_{\alpha=1}^{m} \int \rho_{\alpha,b} U_{\alpha,b}^{\text{ff}} d\mathbf{r} = \frac{V}{2} \sum_{\alpha=1}^{m} \rho_{\alpha,b} U_{\alpha,b}^{\text{ff}},$$
(17)

where V is the volume of the mixture in the bulk phase.

Since the system is in equilibrium with the corresponding bulk mixture, the excess chemical potential in Eq. (14) is equal to the bulk excess chemical potential. The bulk excess chemical potential of each fluid component is defined as

$$\mu_{\alpha,b}^{\text{ex}} = \left. \frac{\partial F_b^{\text{ex}}}{\partial N_{\alpha,b}} \right|_T,\tag{18}$$

where $N_{\alpha,b}$ is the number of molecules of component α in the bulk phase. Using Eqs. (17) and (18), it is easy to show that $\mu_{\alpha,b}^{\text{ex}} = U_{\alpha,b}^{\text{ff}}$ and by substituting $V_{\alpha}^{\text{ext}}(\mathbf{r}) = U_{\alpha}^{\text{wf}}(\mathbf{r})$, Eq. (14) can be re-written in terms of EQT formulation,

$$\rho_{\alpha}(\mathbf{r}) = \rho_{\alpha,b} \exp\left(-\beta \left[U_{\alpha}^{\text{wf}}(\mathbf{r}) + U_{\alpha}^{\text{ff}}(\mathbf{r}) - U_{\alpha,b}^{\text{ff}}\right]\right).$$
(19)

Using Eq. (19), density distribution for each species can be obtained using a numerical procedure such as Picard iteration with the bulk densities as initial guesses.

III. SIMULATION DETAILS

To demonstrate the applicability of the EQT-cDFT approach for confined fluid mixtures, we simulate a confined mixture of hydrogen and methane in graphitic slit pores of various widths in equilibrium with a bulk reservoir. Here, we consider two bulk mixture compositions: methane-rich $(x_m = 0.7)$ and hydrogen-rich bulk mixtures $(x_m = 0.3)$ with a total bulk density of 17.73 atoms/nm³. Methane and hydrogen molecules are modeled as single-site LJ spherical particles. Thus, the standard 12-6 LJ potential is used for both wall-fluid and fluid-fluid interactions with interaction parameters given in Table I.⁴⁹ The Lorentz-Berthelot combination rules are applied for all unlike interactions.

Slit pores consist of two graphene layers separated in the z-direction. The lateral dimensions of the layers in the x-y plane are $3.834 \times 3.689 \text{ nm}^2$ and separation distance, *H*, between the two sheets is varied from 0.762 nm (= $2\sigma_{22}$, where σ_{22} is the length-scale parameter for LJ interaction between methane molecules) to 6.34 nm. Wall atoms are kept fixed throughout the simulation. The spherical cutoff used for Lennard-Jones interactions is 1.6 nm. Periodic boundary conditions are applied in all the directions with an extra vacuum of 6 nm in the z-direction (perpendicular to the

TABLE I. LJ potential parameters for wall atom (C), hydrogen (H_2) , and methane (CH_4) molecules.

Interaction sites	σ (nm)	ϵ (kJ/mol)
C–C	0.340	0.2328
H_2-H_2	0.2915	0.3159
CH ₄ CH ₄	0.381	1.2314

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FIG. 1. Correlation-correction potentials for $x_m = 0.3$ (a) and $x_m = 0.7$ (b) bulk compositions. Solid lines represent same component interactions: CH₄-CH₄ (black) and H₂-H₂ (red); dashed lines stand for cross interactions: CH₄-H₂ (black) and H₂-CH₄ (red).

graphene layers). MD simulations for confined methanehydrogen mixture are performed in GROMACS.⁵⁰ To maintain the temperature at 300 K, Nosé–Hoover thermostat is used with a time constant of 0.2 ps. All systems are equilibrated for 5 ns in the NVT (canonical) ensemble. Following the equilibration, production run for 15 ns is performed with 1 fs time step. As mentioned in Sec. I, the average concentration in the channels can be predicted by the EQT-cDFT approach. To examine this in MD simulations, linear superposition approximation (LSA)⁵¹ method is adopted to estimate the number of molecules inside the channels of width larger than 1.524 nm (= $4\sigma_{22}$). It has been shown that LSA results are in constant chemical potential except at very small separations (about two molecular diameters).⁵² Hence, for pores smaller than $4\sigma_{22}$, the EQT-cDFT results are verified by NVT simulation of slit channels in contact with bulk mixture.⁵³ The distance between walls, densities, and correlation-correction potentials is made dimensionless based on hydrogen LJ



FIG. 2. Comparison of the density profiles of methane and hydrogen from EQT-cDFT and MD simulations at T = 300 K for various channel widths in equilibrium with hydrogen rich bulk mixture ($x_m = 0.3$): (a) 0.762 nm, (b) 1.143 nm, (c) 1.524 nm, (d) 2.25 nm, (e) 3.21 nm, and (f) 6.34 nm. In all insets, circles are MD and lines are EQTcDFT simulation results in which red and black colors denote hydrogen and methane densities, respectively.

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FIG. 3. Comparison of the density profiles of methane and hydrogen from EQT-cDFT and MD simulations at T = 300 K for various channel widths in equilibrium with methane rich bulk mixture ($x_m = 0.7$): (a) 0.762 nm, (b) 1.143 nm, (c) 1.524 nm, (d) 2.25 nm, (e) 3.21 nm, and (f) 6.34 nm. In all insets, circles are MD and lines are EQTcDFT simulation results in which red and black colors denote hydrogen and methane densities, respectively.

parameters $(\sigma_{11}, \epsilon_{11})$ and represented by $z^* = z/\sigma_{11}$, $\rho_{\alpha}^* = \rho_{\alpha}\sigma_{11}^3$, and $\left(u_{\text{ccp, }\alpha\beta}^{\text{ff}}\right)^* = u_{\text{ccp, }\alpha\beta}^{\text{ff}}/\epsilon_{11}$, respectively. In the EQT-cDFT simulations, for fluid-fluid and wall-

In the EQ1-cDF1 simulations, for fluid-fluid and wallfluid Lennard-Jones potentials, the same interaction parameters as in MD simulations are used. Modeling correlationcorrection potential using B-splines (Eq. (8)) gives flexibility to the correction function and provides a numerically robust way of obtaining accurate density profiles. The B-splines knot values for the correlation-correction potentials are optimized based on the potential of mean force (PMF) matching technique,¹⁵ in which the mean-square error in density is minimized such that it reproduces the target potential of mean force within the specified tolerance. In PMF matching, for a slit-like system, where the fluid inhomogeneity is in one direction (z), optimization function for each fluid component is defined as

$$\epsilon_{\alpha} = \frac{1}{2H} \int_{0}^{H} \left(\rho_{\alpha,b} \exp\left(-\beta \tilde{U}_{\alpha}(z)\right) - \rho_{\alpha}^{\text{tgt}}(z) \right)^{2} dz, \quad (20)$$

where $\rho_{\alpha}^{\text{tgt}}$ is the target density of component α , obtained from the reference all-atom MD simulations and \tilde{U}_{α} is defined as

$$\tilde{U}_{\alpha}(z) = U_{\alpha}^{\text{wf}}(z) + U_{\alpha}^{\text{ff}}(z) - U_{\alpha,b}^{\text{ff}}.$$
(21)

To obtain the optimal knot values in correction-correlation function, Eq. (20) is minimized using the Newton-Raphson optimization technique. Further details on PMF matching technique and Newton-Raphson optimization procedure can be found in Ref. 15.

There is no limitation to EQT in terms of system complexity. It has been shown that EQT can also capture density variation of polar molecules such as water in nanoconfined channels.¹⁵ In fact, EQT framework provides a tool to use particle-based coarse-grained potentials for which the electrostatic effects are already embedded.

IV. RESULTS AND DISCUSSION

First, we optimize methane-methane, methane-hydrogen, hydrogen-hydrogen, and hydrogen-methane correlationcorrection potentials for each bulk mixture composition considered in this work. For each bulk mixture composition, PMF-matching-based optimization is performed using the methane and hydrogen density profiles in 6.34 nm channel, which are obtained from the reference MD simulations. We choose 6.34 nm channel for optimization because it is

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large enough that the layered structure and bulk region are well formed for both hydrogen and methane. Fig. 1 shows the optimized $(u_{ccp}^{ff})^*$ for different fluid-fluid interactions. Although, correlation-correction potentials are optimized for a reference channel of 6.34 nm width, we find that they are transferrable across different pores at the same thermodynamic state.

Figs. 2 and 3 depict that the density profiles from the quasi-continuum framework agree well with the MD simulations. In all cases, except for the hydrogen density profile in the smallest channel of methane bulk composition of 0.3 (see Fig. 2(a)), the EQT-cDFT predictions are almost as accurate as MD. Both methane and hydrogen molecules arrange in layers and exhibit an oscillatory structural behavior due to the interplay of wall-fluid and fluid-fluid interactions. Well-formed layered structure and a plateau bulk region are observed for both hydrogen and methane in 6.34 nm channel, which is the largest channel considered in this study (see Figs. 2(f) and 3(f)). Layering is enhanced as the bulk composition increases from 0.3 to 0.7 (see Figs. 2(d)-2(f) and 3(d)-3(f)). This fact is more evident by comparing number of distinct density layers for methane and hydrogen in slits of width 3.21 nm. For a bulk composition of 0.3, the number of distinct layers for methane and hydrogen is 6 (see Fig. 2(e)), whereas for a bulk mixture of 0.7, methane and hydrogen molecules are arranged in 8 layers (see Fig. 3(e)). Thus, increasing methane mole fraction enhances the structural order for both methane and hydrogen. Finally, by comparing the magnitude of the first peak for methane and hydrogen densities, it is evident that methane molecules are more concentrated in the vicinity of the wall. We have also tested the accuracy of the EQT-cDFT approach at lower temperatures of 200 K and 250 K. We found that the density profiles from EQTcDFT approach are in good agreement with MD simulations.

The essential new feature for mixtures is the change in composition due to confinement. Depending on the width, structure, and material, nanopore may become selective towards a certain fluid component in the mixture. For a binary system, the selectivity (*S*) is often expressed as^{5,22,54,55}

$$S = \frac{x_{\alpha,p}/(1 - x_{\alpha,p})}{x_{\alpha,b}/(1 - x_{\alpha,b})},$$
 (22)

where $x_{\alpha,p}$ and $x_{\alpha,b}$ represent the mole fraction of fluid component α in the pore and the coexisting bulk phase, respectively. For a slit channel of width *H*, the average mole fraction for a fluid component α inside the pore can be calculated from the following equation:

$$x_{\alpha,p} = \frac{\int_0^H \rho_\alpha(z) dz}{\sum_{\alpha=1}^2 \int_0^H \rho_\alpha(z) dz}.$$
 (23)

Fig. 4 shows the selectivity of methane relative to hydrogen at T = 300 K as a function of pore width, for channels in equilibrium with the hydrogen-rich bulk reservoir ($x_m = 0.3$). It can be seen that the agreement between the MD and EQT-cDFT results is good. In Fig. 4, *S* values greater than unity represent that the channel is completely selective toward methane. It can be seen that methane shows a higher adsorption affinity than hydrogen, especially in the smaller pores. This



FIG. 4. Selectivity of methane over hydrogen as a function of channel width.

is due to the larger interaction energy between methane and graphene than hydrogen. The same line of reasoning has also been used in other literature^{56,57} in which they have shown that the molar fraction of the component having the strongest interaction with the channel is increased compared to the bulk.

V. CONCLUSION

EQT is a practical, fast, and easy approach to bridge the gap between atomistic and continuum methods by constructing potentials from atomistic interactions. These potentials can be used in a continuum framework such as the Nernst-Planck equation or to construct a grand potential functional within the classical density functional theory framework (EQT-cDFT). In the present study, we demonstrated the EQTcDFT method by predicting density distributions of methane and hydrogen mixtures confined in graphitic nanopores of various widths. We considered two extreme cases, where channels are in equilibrium with methane-rich and hydrogenrich bulk mixtures. In both cases, theoretical results compare well with the MD simulations. We also used EQT-cDFT results to calculate adsorption selectivity of the mixture rich in hydrogen. It is found that though the bulk composition favors hydrogen, graphene slit channels exhibit selectivity for methane molecule. This finding can be attributed to the larger energy interaction of methane and graphene wall. EQTcDFT is a promising multiscale framework that can accurately predict structure and other thermodynamic properties of confined fluids.

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- ¹T. Thorsen, S. J. Maerkl, and S. R. Quake, Science 298, 580 (2002).
- ²C. A. Miller and P. Neogi, *Interfacial Phenomena: Equilibrium and Dynamic Effects* (CRC Press, 2007).
- ³P. T. Cummings, H. Docherty, C. R. Iacovella, and J. K. Singh, AIChE J. **56**, 842 (2010).
- ⁴C. Smith, Nature **446**, 219 (2007).
- ⁵L. D. Gelb, K. E. Gubbins, R. Radhakrishnan, and M. Sliwinska-Bartkowiak, Rep. Prog. Phys. 62, 1573 (1999).
- ⁶R. Bhadauria and N. R. Aluru, J. Chem. Phys. 139, 074109 (2013).
- ⁷B. A. Dalton, P. J. Daivis, J. S. Hansen, and B. D. Todd, Phys. Rev. E 88, 052143 (2013).
- ⁸B. K. Peterson, K. E. Gubbins, G. S. Heffelfinger, U. M. B. Marconi, and F. van Swol, J. Chem. Phys. 88, 6487 (1988).
- ⁹R. Qiao and N. R. Aluru, J. Chem. Phys. 118, 4692 (2003).
- ¹⁰R. Qiao and N. Aluru, Phys. Rev. Lett. **92**, 198301 (2004).
- ¹¹A. V. Raghunathan, J. H. Park, and N. R. Aluru, J. Chem. Phys. **127**, 174701 (2007).
- ¹²T. Sanghi and N. R. Aluru, J. Chem. Phys. **132**, 044703 (2010).
- ¹³T. Sanghi and N. R. Aluru, J. Chem. Phys. 136, 024102 (2012).
- ¹⁴S. Y. Mashayak and N. R. Aluru, J. Chem. Theory Comput. **8**, 1828 (2012).
- ¹⁵S. Y. Mashayak and N. R. Aluru, J. Chem. Phys. **137**, 214707 (2012).
- ¹⁶J. Wu, AIChE J. **52**, 1169 (2006).
- ¹⁷R. Evans, *Lecture Notes* (3rd Warsaw School of Statistical Physics, 2009), Vol. 27.
- ¹⁸K. E. Gubbins, Y.-C. Liu, J. D. Moore, and J. C. Palmer, Phys. Chem. Chem. Phys. **13**, 58 (2011).
- ¹⁹C. Ebner, W. Saam, and D. Stroud, Phys. Rev. A 14, 2264 (1976).
- ²⁰E. Kierlik and M. L. Rosinberg, Phys. Rev. A 44, 5025 (1991).
- ²¹E. Kierlik, Y. Fan, P. A. Monson, and M. L. Rosinberg, J. Chem. Phys. **102**, 3712 (1995).
- ²²M. Sliwinska-Bartkowiak, R. Sikorski, S. L. Sowers, L. D. Gelb, and K. E. Gubbins, Fluid Phase Equilib. **136**, 93 (1997).
- ²³F.-Q. You, Y.-X. Yu, and G.-H. Gao, J. Phys. Chem. B 109, 3512 (2005).
- ²⁴Y.-X. Yu, F.-Q. You, Y. Tang, G.-H. Gao, and Y.-G. Li, J. Phys. Chem. B 110, 334 (2006).
- ²⁵F.-Q. You, Y.-X. Yu, and G.-H. Gao, J. Chem. Phys. **123**, 114705 (2005).
- ²⁶F. van Swol and J. R. Henderson, Phys. Rev. A **43**, 2932 (1991).
- ²⁷B. Peng and Y.-X. Yu, J. Phys. Chem. B **112**, 15407 (2008).
- ²⁸B. Peng and Y.-X. Yu, Langmuir **24**, 12431 (2008).
- ²⁹N. Choudhury and S. K. Ghosh, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys. 64, 021206 (2001).

- ³⁰Y. Tang and J. Wu, J. Chem. Phys. **119**, 7388 (2003).
- ³¹Y.-X. Yu, G.-H. Gao, and X.-L. Wang, J. Phys. Chem. B **110**, 14418 (2006).
- ³²J. Puibasset, E. Kierlik, and G. Tarjus, J. Chem. Phys. 141, 044716 (2014).
- ³³S. Y. Mashayak, M. H. Motevaselian, and N. R. Aluru, J. Chem. Phys. 142, 244116 (2015).
- ³⁴J. A. Barker and D. Henderson, J. Chem. Phys. 47, 4714 (1967).
- ³⁵J. Lebowitz, Phys. Rev. 133, A895 (1964).
- ³⁶P. J. Leonard, D. Henderson, and J. A. Barker, Mol. Phys. 21, 107 (1971).
- ³⁷C. Caccamo, Phys. Rep. **274**, 1 (1996).
- ³⁸Y. Rosenfeld, Phys. Rev. Lett. **63**, 980 (1989).
- ³⁹Y. Rosenfeld, J. Chem. Phys. **98**, 8126 (1993).
- ⁴⁰R. Roth, J. Phys.: Condens. Matter **22**, 063102 (2010).
- ⁴¹Y.-X. Yu and J. Wu, J. Chem. Phys. **117**, 2368 (2002).
- ⁴²R. Roth, R. Evans, A. Lang, and G. Kahl, J. Phys.: Condens. Matter 14, 12063 (2002).
- ⁴³Y.-X. Yu, J. Wu, Y.-X. Xin, and G.-H. Gao, J. Chem. Phys. **121**, 1535 (2004).
 ⁴⁴Y.-X. Yu, J. Chem. Phys. **131**, 024704 (2009).
- ⁴⁵G. J. Gloor, G. Jackson, F. J. Blas, E. M. delRio, and E. deMiguel, J. Phys. Chem. C 111, 15513 (2007).
- ⁴⁶J. Hughes, E. J. Krebs, and D. Roundy, J. Chem. Phys. **138**, 024509 (2013).
- ⁴⁷K. Gong, B. D. Marshall, and W. G. Chapman, J. Chem. Phys. **139**, 094904 (2013).
- ⁴⁸E. Krebs, J. Schulte, and D. Roundy, J. Chem. Phys. **140**, 124507 (2014).
- ⁴⁹S. Bhatia and D. Nicholson, Phys. Rev. Lett. **100**, 236103 (2008).
- ⁵⁰B. Hess, C. Kutzner, D. van der Spoel, and E. Lindahl, J. Chem. Theory Comput. 4, 435 (2008).
- ⁵¹I. K. Snook and W. van Megen, J. Chem. Phys. **72**, 2907 (1980).
- ⁵²S. K. Das, M. M. Sharma, and R. S. Schechter, J. Phys. Chem. **100**, 7122 (1996).
- ⁵³E. Spohr, A. Trokhymchuk, and D. Henderson, J. Electroanal. Chem. 450, 281 (1998).
- ⁵⁴M. Gallo, T. M. Nenoff, and M. C. Mitchell, Fluid Phase Equilib. 247, 135 (2006).
- ⁵⁵C. Gu, G.-H. Gao, Y.-X. Yu, and T. Nitta, Fluid Phase Equilib. **194-197**, 297 (2002).
- ⁵⁶R. F. Cracknell, D. Nicholson, S. R. Tennison, and J. Bromhead, Adsorption 2, 193 (1996).
- ⁵⁷B. Coasne, J. Czwartos, M. Sliwinska-Bartkowiak, and K. E. Gubbins, J. Chem. Phys. **133**, 084701 (2010).