Coarse-grained potential models for structural prediction of carbon dioxide (CO$_2$) in confined environments

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(Received 8 September 2011; accepted 14 December 2011; published online 9 January 2012)

In this paper, we propose coarse-grained single-site (CGSS), wall-CO$_2$, and CO$_2$-CO$_2$ interaction potential models to study the structure of carbon dioxide under confinement. The CGSS potentials are used in an empirical potential based quasi-continuum theory, EQT, to compute the center-of-mass density and potential profiles of CO$_2$ confined inside different size graphite slit pores. Results obtained from EQT are compared with those obtained from all-atom molecular dynamics (AA-MD) simulations, and are found to be in good agreement with each other. Though these CGSS interaction potentials are primarily developed and parameterized for EQT, they are also used to perform coarse-grained molecular dynamics (CG-MD) simulations. The results obtained from CG-MD simulations are also found to be in reasonable agreement with AA-MD simulation results.


I. INTRODUCTION

Geological storage of carbon dioxide is a promising option to reduce the level of carbon dioxide in the atmosphere and mitigate its effect on climate change. In geological storage, high pressure carbon dioxide is injected into the underground porous rock formations, where it gets trapped inside the tiny nanometer size pores of the rocks. Thus, a good understanding of the microstructure of carbon dioxide inside nanoscale confinements is of great practical importance in developing an efficient technology for carbon dioxide storage.

In recent decades, computer simulations have become a powerful tool to investigate the properties of molecules under nanoscale confinement. There exist several molecular simulation methods such as molecular dynamics (MD) and Monte Carlo (MC) simulations that can be used to study fluid confinement at nanometer scale. These methods require interatomic potentials (force-fields) that describe the interaction among the molecules as input. The accuracy of the results obtained from these methods is highly dependent on the physical correctness of the interaction potentials. Though MD and MC simulations have been extensively used to study fluid confinement at nanometer scale, both require enormous computing resources, which practically limit their use to simulate systems on smaller length and time scales. Hence, in recent years, a large amount of effort has been devoted in developing novel simulation approaches that allow computationally efficient simulation across bigger spectrum of length and time scales. Coarse-graining and multi-scale methods are two fast emerging concepts used to simulate large and complex systems over longer length and time scales. In coarse-graining, a reduced-order representation of the actual system is constructed, and a coarse-grained (CG) interaction potential is developed that permits the use of a bigger time step for stable simulations. Multi-scale methods attempt to combine the atomic-scale and macro-scale methods and provide a unified framework to study the fluid behavior across multiple length and time scales.

Over the years, several potential models have been proposed to represent carbon dioxide. Most of these models can be categorized into two sub-groups: (1) All atom site-site potentials in which carbon dioxide is modeled as a rigid two/three site Lennard-Jones (LJ) molecule with quadrupole moment either stated explicitly or decomposed into partial charges. These models are computationally quite expensive, but provide a fairly accurate description of the structural properties of carbon dioxide, both in the bulk and under confinement. (2) Single-site LJ type potentials; these are CG potentials which have the great advantage of computational efficiency, but they typically lose the microscopic structural information related to the shape of the molecule. Though, several CG potentials are developed that reproduce the bulk properties of carbon dioxide quite well, not much attention has been given to the development of the CG potentials to study the structural properties of carbon dioxide in confined environments. Furthermore, it has been reported that the usage of the single-site CG potentials developed for the bulk state do not predict the correct microstructure of carbon dioxide under high-pressure confinement. Most of the confinement studies on carbon dioxide are still performed using the computationally expensive all atom site-site potentials. The aim of this work is to develop CGSS wall-CO$_2$ and CO$_2$-CO$_2$ interaction potentials that can be used in empirical potential based quasi-continuum theory, EQT, to study the structure of carbon dioxide under confinement. In EQT, one-dimensional steady-state Nernst-Planck (NP) equation is derived:

\[
\frac{d}{dz} \left( \frac{dc}{dz} + \frac{c}{RT} \frac{dU}{dz} \right) = 0, \tag{1}
\]
with boundary conditions
\[ c(z = 0) = 0, \]
\[ c(z = L) = 0, \]
\[
\frac{1}{L} \int_0^L c(z) \, dz = c_{\text{avg}}, \tag{2}
\]
is solved to obtain self-consistent potential and concentration profiles of the confined fluid. Here, \( c \) is the fluid concentration (we also use the notation \( c_{\text{CO}_2} \) to refer to it), \( R \) is the gas constant, \( T \) is the temperature, and \( U \) is the potential of mean force (PMF) profile of the confined fluid. \( L \) is the dimension of the confining geometry and \( c_{\text{avg}} \) is the average concentration of the confined fluid. The central task in EQT is the development of the quasi-continuum potential models to compute the PMF profile, \( U \), of the confined fluid. The quasi-continuum potentials are developed using the inter-atomic potentials that describe the interactions between the molecules at atomistic scale. This approach embeds the atomistic scale physics into a continuum scale framework and provides a means to capture both the interfacial (non-continuum inhomogeneous behavior) and the bulk structure (homogeneous behavior) of the confined fluid. We use CGSS inter-molecular potentials proposed in this work to develop quasi-continuum potential models for carbon dioxide. The mathematical simplicity and the computational efficiency of EQT makes it a promising coarse-grained multi-scale approach to study the structure of confined fluids. Further details on EQT can be found in Refs. 15 and 16.

The remainder of the paper is organized as follows. In Sec. II, we first propose the functional form for CGSS wall-CO\(_2\) and CO\(_2\)-CO\(_2\) interaction potentials, and discuss their parameterization procedure. Then, we discuss the transferability of the functional form of CGSS potentials across different thermodynamic states. In Sec. III, we use the CGSS inter-molecular potentials to develop quasi-continuum potential models for carbon dioxide. Simulation details are provided in Sec. IV. In Sec. V, we use the quasi-continuum potential models in EQT to compute the center-of-mass (COM) density profiles of carbon dioxide confined inside different size graphite slit pores. The results obtained from EQT are compared with those obtained from all-atom molecular dynamics (AA-MD) simulations. Though these CGSS inter-molecular potentials are primarily developed and parameterized for EQT, they are also used to perform coarse-grained molecular dynamics (CG-MD) simulations. The objective is to check their performance in a particle based CG simulation method. The results obtained from CG-MD simulations are also reported in Sec. V. Finally, conclusions are presented in Sec. VI.

II. COARSE-GRAINED SINGLE-SITE INTER-MOLECULAR INTERACTION POTENTIALS

A. Functional form

The specification of the functional form of the interaction potential is one of the most important and challenging tasks in the process of coarse-graining.\(^3,4\) A good CG potential should have a simple functional form with physically meaningful coarse-graining parameters and a wide range of transferability. Typically, the specification of the functional form is guided by the understanding of the physics of the problem. We coarse-grain CO\(_2\) as a single-site spherical bead placed at its COM position. To propose the functional form for CGSS wall-CO\(_2\) and CO\(_2\)-CO\(_2\) interaction potentials, we first discuss the microstructure of carbon dioxide molecules under confinement. Figures 1(a) and 1(b) show the COM density profile, \( \rho(z) \), and the molecular orientation profile, \( S_\theta \), of supercritical carbon dioxide \((T = 323 \text{ K} \text{ and } P = 10.1 \text{ MPa}; \text{critical temperature}, T_c \approx 304 \text{ K} \text{ and critical pressure}, P_c \approx 7.3 \text{ MPa})\) confined inside a 2.232 nm wide graphite slit pore (slit is infinite in \( x \) and \( y \) directions), respectively. The average number density of the carbon dioxide molecules in the pore is 9.0 molecules/nm\(^3\).\(^{17,18}\) The density profile, \( \rho(z) \), is computed as

\[ \rho(z) = \frac{\langle N(z) \rangle}{L_x L_y \Delta z}. \tag{3} \]

Here, \( L_x (4.550 \text{ nm}) \) and \( L_y (4.331 \text{ nm}) \) are the lateral dimensions of the graphite slit, \( N(z) \) are the number of CO\(_2\) molecules for which the COM lies in the bin \([z, z + \Delta z]\) and \( \langle \cdots \rangle \) denotes the ensemble average. The bin size, \( \Delta z \), is taken as 0.01 nm. The molecular orientation is computed using the order parameter \( S_\theta \) defined as

\[ S_\theta = \frac{3\langle \cos^2 \theta \rangle - 1}{2}. \tag{4} \]

Here, \( \theta \) is the angle between the molecular axis and a normal vector through the walls. The order parameter takes a value of \(-0.5\) if molecules are aligned parallel to the wall, a value of 1 if the molecules are aligned perpendicular to the wall, and a value of 0 if they are randomly oriented. Further, to understand the effect of the wall-fluid and the fluid-fluid interactions separately, we divide the confining geometry into two regions. The region up to 0.5 nm from the walls \((z \leq 0.5 \text{ nm} \text{ and } z \geq 1.732 \text{ nm})\), where the wall-fluid interactions are the dominant interactions, is defined as the interfacial region and the remaining region is defined as the central region of the pore or slit. It can be observed from Figures 1(a) and 1(b) that the density profile in the interfacial region is split into two sub-layers and each corresponds to a different preferred molecular orientation. In the first sub-layer, the order parameter is less than zero \((S_\theta \approx -0.4)\) and molecules are aligned parallel to the wall, while in the second sub-layer the order parameter is greater than zero \((S_\theta \approx 0.2)\) indicating that the molecules are rotated with respect to the wall. To capture this orientation dependent arrangement of molecules in the interfacial region, we use piecewise interaction functions and define the wall-CO\(_2\) interaction potential as (see Fig. 2(a))
FIG. 1. (a) COM density profile, (b) molecular orientation profile, (c) relative orientation profile of supercritical carbon dioxide \((T = 323\text{ K}, P = 10.1\text{ MPa})\) confined inside a 2.232 nm wide graphite slit pore, (d) COM coordinates used to study the relative orientation of two carbon dioxide molecules.

\[
\begin{align*}
\mathcal{U}_{\text{wall-CO}_2}^{\text{CGSS}}(r) &= \begin{cases} 
\mathcal{U}_{\text{LJ}}(r, \sigma_1, \epsilon_1) & r \leq R_{\text{trans}} \\
\mathcal{U}_{\text{LJ}}(r, \sigma_1, \epsilon_1) + c_1 \mathcal{U}_{\text{LJ}}(r, \sigma_2, \epsilon_2) + c_2 \mathcal{U}_{\text{LJ}}(r, \sigma_2, \epsilon_2) & R_{\text{trans}} < r \leq R_{\text{trans}} + \Delta, \\
\mathcal{U}_{\text{LJ}}(r, \sigma_2, \epsilon_2) & r > R_{\text{trans}} + \Delta
\end{cases}
\end{align*}
\]  
(5)

where \(\mathcal{U}_{\text{LJ}}(r, \sigma, \epsilon)\) is defined as

\[
\mathcal{U}_{\text{LJ}}(r, \sigma, \epsilon) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}, \quad i = 1, 2.
\]  
(6)

Here, \(r\) is the distance between the wall atom and the CG CO\(_2\) molecule, \(\sigma_i\) and \(\epsilon_i\) are the distance and the energy parameters, respectively. The first region is a 12–6 LJ potential up to \(R_{\text{trans}}\) to model the interaction of the wall atoms with the CO\(_2\) molecules in the first sub-layer. The second region is a linear superposition of two 12–6 LJ potentials, and operates at separation distances greater than \(R_{\text{trans}} + \Delta\) to model the interaction of the wall atoms with the CO\(_2\) molecules in the second sub-layer. \(c_1\) and \(c_2\) are two constants that control the contribution of the two 12–6 LJ potentials in the second region. The two regions are connected by a polynomial bridge function of width \(\Delta\). The coefficients \(a_0, a_1, a_2,\) and \(a_3\) of the bridge function are computed to ensure smooth transition of the potential (continuity of the potential and its first derivative) at \(R_{\text{trans}}\) and \(R_{\text{trans}} + \Delta\).

For fluid-fluid interactions, the oscillation of the molecular orientation profile (Fig. 1(b)) in the interfacial and the central region suggests different preferred orientation across the density layers. Under high pressure (or high density) confinement, the molecules arrange themselves into layers which are rotated relative to each other. This type of arrangement occurs because of the linear shape of the carbon dioxide molecule.
and results in the most efficient packing under confinement. To define the interaction among the fluid molecules, we plan to use the same functional form as proposed for the wall-CO$_2$ interactions. Though this molecular orientation analysis guides us to define the functional form for the fluid-fluid interaction potential, it does not provide any information on the relative orientation of the two fluid molecules, which could be different in the interfacial and the central region. This information on the relative orientation is required to understand if one uniform fluid-fluid potential could be used across the entire length of the confinement. If the relative orientation profile is different in the two regions, then one would have to define a separate potential for each region. Figure 1(c) shows the relative orientation profile of carbon dioxide molecules in the interfacial (solid line) and the central (broken line) region of the confinement. The relative orientation is defined in the COM coordinates $r_{\text{COM}}, \theta_1, \theta_2,$ and $\phi$ (see Fig. 1(d)). $r_{\text{COM}}$ is the separation between the COM of the two molecules, $\theta$ is the angle made by the molecular axis of each molecule with the $r_{\text{COM}}$ and $\phi$ is the dihedral angle between the two planes defined by the $r_{\text{COM}}$ and the molecular axis for each molecule. It can be observed that the relative orientation profile in the interfacial region is not significantly different from that in the central region ($\Delta \theta_1 \simeq 7^\circ$, $\Delta \theta_2 \simeq 7^\circ$, $\Delta \phi \simeq 3^\circ$; $\Delta \theta_1$, $\Delta \theta_2$, and $\Delta \phi$ are the difference between the values of $\theta_1$, $\theta_2$, and $\phi$ in the interfacial and the central region, respectively). Thus, we specify one uniform interaction potential and define the CO$_2$-CO$_2$ interaction potential as

$$u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}(r) = \begin{cases} u_{LJ}(r, \sigma_1, \epsilon_1) & r \leq R_{\text{trans}} \\ a_0 + a_1r + a_2r^2 + a_3r^3 & R_{\text{trans}} < r \leq R_{\text{trans}} + \Delta \\ c_1u_{LJ}(r, \sigma_1, \epsilon_1) + c_2u_{LJ}(r, \sigma_2, \epsilon_2) & r > R_{\text{trans}} + \Delta \end{cases} \quad (7)$$

Here, $r$ is the distance between the two CG CO$_2$ molecules. All other functions and parameters have the same meaning as defined above for $u_{\text{CGSS}}^{\text{wall-CO}_2}$.

B. Parameterization

Once the functional form is specified, the next step is the parameterization of the potential to reproduce the property of interest, commonly referred to as the target function in the coarse-graining literature. We parameterize the interfacial (solid line) and the central (broken line) region of the confinement. The relative orientation is defined in the COM coordinates $r_{\text{COM}}, \theta_1, \theta_2,$ and $\phi$ (see Fig. 1(d)). $r_{\text{COM}}$ is the separation between the COM of the two molecules, $\theta$ is the angle made by the molecular axis of each molecule with the $r_{\text{COM}}$ and $\phi$ is the dihedral angle between the two planes defined by the $r_{\text{COM}}$ and the molecular axis for each molecule. It can be observed that the relative orientation profile in the interfacial region is not significantly different from that in the central region ($\Delta \theta_1 \simeq 7^\circ$, $\Delta \theta_2 \simeq 7^\circ$, $\Delta \phi \simeq 3^\circ$; $\Delta \theta_1$, $\Delta \theta_2$, and $\Delta \phi$ are the difference between the values of $\theta_1$, $\theta_2$, and $\phi$ in the interfacial and the central region, respectively). Thus, we specify one uniform interaction potential and define the CO$_2$-CO$_2$ interaction potential as

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Here, $r$ is the distance between the two CG CO$_2$ molecules. All other functions and parameters have the same meaning as defined above for $u_{\text{CGSS}}^{\text{wall-CO}_2}$.

B. Parameterization

Once the functional form is specified, the next step is to define the interaction among the fluid molecules, we plan to use the same functional form as proposed for the wall-CO$_2$ interactions. Though this molecular orientation analysis guides us to define the functional form for the fluid-fluid interaction potential, it does not provide any information on the relative orientation of the two fluid molecules, which could be different in the interfacial and the central region. This information on the relative orientation is required to understand if one uniform fluid-fluid potential could be used across the entire length of the confinement. If the relative orientation profile is different in the two regions, then one would have to define a separate potential for each region. Figure 1(c) shows the relative orientation profile of carbon dioxide molecules in the interfacial (solid line) and the central (broken line) region of the confinement. The relative orientation is defined in the COM coordinates $r_{\text{COM}}, \theta_1, \theta_2,$ and $\phi$ (see Fig. 1(d)). $r_{\text{COM}}$ is the separation between the COM of the two molecules, $\theta$ is the angle made by the molecular axis of each molecule with the $r_{\text{COM}}$ and $\phi$ is the dihedral angle between the two planes defined by the $r_{\text{COM}}$ and the molecular axis for each molecule. It can be observed that the relative orientation profile in the interfacial region is not significantly different from that in the central region ($\Delta \theta_1 \simeq 7^\circ$, $\Delta \theta_2 \simeq 7^\circ$, $\Delta \phi \simeq 3^\circ$; $\Delta \theta_1$, $\Delta \theta_2$, and $\Delta \phi$ are the difference between the values of $\theta_1$, $\theta_2$, and $\phi$ in the interfacial and the central region, respectively). Thus, we specify one uniform interaction potential and define the CO$_2$-CO$_2$ interaction potential as

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Here, $r$ is the distance between the two CG CO$_2$ molecules. All other functions and parameters have the same meaning as defined above for $u_{\text{CGSS}}^{\text{wall-CO}_2}$.

B. Parameterization

Once the functional form is specified, the next step is the parameterization of the potential to reproduce the property of interest, commonly referred to as the target function in the coarse-graining literature. We parameterize

$$u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}(r) = \begin{cases} u_{LJ}(r, \sigma_1, \epsilon_1) & r \leq R_{\text{trans}} \\ a_0 + a_1r + a_2r^2 + a_3r^3 & R_{\text{trans}} < r \leq R_{\text{trans}} + \Delta \\ c_1u_{LJ}(r, \sigma_1, \epsilon_1) + c_2u_{LJ}(r, \sigma_2, \epsilon_2) & r > R_{\text{trans}} + \Delta \end{cases} \quad (7)$$

Here, $r$ is the distance between the two CG CO$_2$ molecules. All other functions and parameters have the same meaning as defined above for $u_{\text{CGSS}}^{\text{wall-CO}_2}$.
Here, \( F_i(\mathbf{r}) \) is the mean force that acts on particle \( i \) (at position \( r \)) due to its interaction with all other particles. \( U_i(r_o) \) is the value of the potential at a reference position \( r_o \). For semi-infinite slit pores considered in this work, the reference position \( r_o \) is taken to be the center of the pore, i.e., \( r_o(x, y, z) = (x, y, H/2); H \) is the slit width. Also, since the slit is infinite in \( x \) and \( y \) directions, only the variation in the \( z \) direction is relevant. To parameterize the potentials for a given thermodynamic state, we first run an AA-MD simulation and compute the wall-fluid and fluid-fluid potentials at position \( z \) due to the wall-fluid (or fluid-fluid) interactions alone. This step can be performed using the table \( 21 \) and rerun option in the mdrun program of the simulation package GROMACS. Then, the CG wall-fluid PMF, \( U_{CGSS\text{-wall-CO}_2}(z) \), and the CG fluid-fluid PMF, \( U_{CGSS\text{-CO}_2-CO}_2(z) \), are computed as

\[
U_{CGSS\text{-wall-CO}_2}(z) = U_{AA\text{-wall-CO}_2}(z_o) - \int_{z_o}^{z} \langle F_{AA\text{-wall-CO}_2}(z') \rangle \, dz',
\]

\[
U_{CGSS\text{-CO}_2-CO}_2(z) = U_{AA\text{-CO}_2-CO}_2(z_o) - \int_{z_o}^{z} \langle F_{AA\text{-CO}_2-CO}_2(z') \rangle \, dz'.
\]

Here, \( \langle F_{AA\text{-wall-CO}_2}(z) \rangle \) and \( \langle F_{AA\text{-CO}_2-CO}_2(z) \rangle \) are the mean force experienced by the molecules at position \( z \) (molecules whose COM lie in the bin \([z, (z + \Delta z)]\)) due to the wall-fluid and fluid-fluid interactions, respectively. \( U_{AA\text{-wall-CO}_2}(z_o) \) and \( U_{AA\text{-CO}_2-CO}_2(z_o) \) are the reference wall-fluid and fluid-fluid potentials at position \( z_o = H/2 \). \( U_{CGSS\text{-wall-CO}_2}(z) \) and \( U_{CGSS\text{-CO}_2-CO}_2(z) \) are the target wall-fluid and fluid-fluid PMF profiles, which we want to reproduce with \( U_{CGSS\text{-wall-CO}_2} \) and \( U_{CGSS\text{-CO}_2-CO}_2 \), respectively. The CG wall-fluid and fluid-fluid PMF profiles are computed following the same procedure as discussed above for the computation of the target PMF profiles. First, the total force experienced by each CG CO\(_2\) molecule (CO\(_2\) is coarse-grained as a spherical bead placed at its COM position) due to the CG wall-fluid and fluid-fluid interactions (defined by \( u_{CGSS\text{-wall-CO}_2}(r) \) and \( u_{CGSS\text{-CO}_2-CO}_2(r) \)) is computed, i.e.,

\[
F_{CG\text{-wall-CO}_2}(r_i^{AA}) = \sum_{j=1}^{N_j} \frac{d}{dr} u_{CGSS\text{-wall-CO}_2}\left( |r_i^{AA} - r_j^{AA}| \right),
\]

\[
F_{CG\text{-CO}_2-CO}_2(r_i^{AA}) = \sum_{j=1}^{N_j} \frac{d}{dr} u_{CGSS\text{-CO}_2-CO}_2\left( |r_i^{AA} - r_j^{AA}| \right).
\]
wall-fluid and fluid-fluid PMF profiles (solid line) with their respective target PMF profiles (open circle) for supercritical carbon dioxide ($T = 323 \text{ K}$ and $P = 10.1 \text{ MPa}$) confined inside a 2.232 nm wide graphite slit pore. The parameters used in the CGSS potentials are reported in Table I. It can be observed that the CG wall-fluid and fluid-fluid PMF profiles match well with their respective target PMF profiles. The proposed functional form for $u_{\text{CGSS}}^{\text{wall-CO}_2}$ captures the two minima in the wall-fluid PMF quite accurately. These two minima cause the splitting of the density profile in the interfacial region into two sub-layers. $u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$ also captures the minima in the fluid-fluid PMF profile quite accurately. These minima positions correspond to the density peaks in the central region of the channel. There is a small error in the magnitude of the CG fluid-fluid PMF profile in the region up to 0.3 nm from the walls. Due to the highly repulsive nature of the wall-fluid PMF in this region ($U_{\text{wall-CO}_2}^{\text{CG}}(z) > 5 K_B T$; $K_B$ is the Boltzmann constant), this error does not affect the structural prediction in the interfacial region. It is important to understand that this parameterization procedure ensures that given a set of equilibrium trajectories, $u_{\text{CGSS}}^{\text{wall-CO}_2}$ and $u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$ will reproduce the wall-fluid and the fluid-fluid PMF profiles of the confined fluid, respectively. It does not guarantee that given any random initial configuration, these potentials would evolve the system to its equilibrium configuration the same way as AA-MD simulation. This issue was checked by using these potentials to perform CG-MD simulations. The CG-MD simulation results are reported in Sec. V.

C. Transferability

To check the transferability of the functional form of $u_{\text{CGSS}}^{\text{wall-CO}_2}$ and $u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$, they were parameterized for four different thermodynamic states ($T = 323 \text{ K}$, $P = 10.1 \text{ MPa}$; $T = 323 \text{ K}$, $P = 1.01 \text{ MPa}$; $T = 348 \text{ K}$, $P = 9.05 \text{ MPa}$; $T = 308 \text{ K}$, $P = 5.5 \text{ MPa}$). The first two states are chosen to check the transferability of the functional form to high and low pressure confinements. The last two states are representative of high pressure confinement at supercritical temperatures. During parameterization, the variation of the coarse-graining parameters was studied to obtain their functional dependence with the thermodynamic variables and associate a physical meaning where ever possible. While parameterizing the wall-fluid interaction potential, $u_{\text{CGSS}}^{\text{wall-CO}_2}$, for high-pressure confinements (pressure values for which the first layer splits into two sub-layers), it was observed that the values of the parameters $\sigma_1$ and $\sigma_2$ were quite close to the distance values at which the two minima occur in the wall-CO$_2$ PMF profile. For the three high-pressure states ($P \geq 5.5 \text{ MPa}$) considered in this work, the first and the second minima occur at $\sim 0.335 \text{ nm}$ and $0.405 \text{ nm}$ away from the wall, respectively. Hence, to parameterize $u_{\text{CGSS}}^{\text{wall-CO}_2}$, the values $\sigma_1 = 0.335 \text{ nm}$ and $\sigma_2 = 0.405 \text{ nm}$ were used and they worked well in all the three high-pressure thermodynamic states. Interestingly, the usage of the same values ($\sigma_1 = 0.335 \text{ nm}$ and $\sigma_2 = 0.405 \text{ nm}$) also worked fine in the parameterization of the fluid-fluid interaction potential, $u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$, for these high-pressure states. Also, for $u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$, it was observed that once it is parameterized for a high-pressure state ($T = 323 \text{ K}$, $P = 10.1 \text{ MPa}$), only the coarse-graining parameter $R_{\text{trans}}$ needs to be changed to re-parameterize it for a low-pressure state at the same temperature ($T = 323 \text{ K}$, $P = 1.01 \text{ MPa}$). The potentials were not found to be physically sensitive to the coarse-graining parameters $\Delta$, $c_1$, and $c_2$, whose variations were mostly considered to fine tune the results. $c_1 = c_2 = 0.5$ and $\Delta$ value in the range of 0.03 to 0.05 nm were found to be working fine for all the four thermodynamic states considered in this study. Figure 4 shows the comparison of the CG wall-fluid PMF, $U_{\text{wall-CO}_2}^{\text{CG}}$, and the CG fluid-fluid PMF, $U_{\text{CO}_2-\text{CO}_2}^{\text{CG}}$ (right) profiles obtained from CGSS potentials (solid line) with their respective target PMF profiles (open circle) at different thermodynamic states. The parameters for the CGSS potentials are obtained following the procedure outlined in Algorithm I, and are reported in Table I. It can be observed that the proposed functional form of $u_{\text{CGSS}}^{\text{wall-CO}_2}$ performs well for all the thermodynamic states and reproduces the wall-fluid PMF quite accurately. The functional form of $u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$ performs better for high pressure (or density) states than for low pressure states. At high densities, short range inter-molecular repulsions are typically the dominant interactions, and $u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$, which is designed as a combination of 12–6 LJ potentials, reproduces the PMF profiles quite accurately. At low densities, long range electrostatic interactions also become important and $u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$ does not capture these long range effects quite efficiently. The

<table>
<thead>
<tr>
<th>Thermodynamic state</th>
<th>Potential</th>
<th>$\sigma_1$ (nm)</th>
<th>$\epsilon_1$ (kJ/mol)</th>
<th>$\sigma_2$ (nm)</th>
<th>$\epsilon_2$ (kJ/mol)</th>
<th>$R_{\text{trans}}$ (nm)</th>
<th>$\Delta$ (nm)</th>
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<tr>
<td>$T = 323 \text{ K}$</td>
<td>$u_{\text{CGSS}}^{\text{wall-CO}_2}$</td>
<td>0.335</td>
<td>0.45</td>
<td>0.405</td>
<td>0.55</td>
<td>0.345</td>
<td>0.05</td>
<td>0.55</td>
<td>0.45</td>
</tr>
<tr>
<td>$P = 10.1 \text{ MPa}$</td>
<td>$u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$</td>
<td>0.335</td>
<td>1.15</td>
<td>0.405</td>
<td>1.75</td>
<td>0.375</td>
<td>0.03</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$T = 348 \text{ K}$</td>
<td>$u_{\text{CGSS}}^{\text{wall-CO}_2}$</td>
<td>0.335</td>
<td>0.45</td>
<td>0.405</td>
<td>0.55</td>
<td>0.345</td>
<td>0.05</td>
<td>0.55</td>
<td>0.45</td>
</tr>
<tr>
<td>$P = 9.05 \text{ MPa}$</td>
<td>$u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$</td>
<td>0.335</td>
<td>1.15</td>
<td>0.405</td>
<td>1.70</td>
<td>0.375</td>
<td>0.03</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$T = 308 \text{ K}$</td>
<td>$u_{\text{CGSS}}^{\text{wall-CO}_2}$</td>
<td>0.335</td>
<td>0.45</td>
<td>0.405</td>
<td>0.55</td>
<td>0.345</td>
<td>0.05</td>
<td>0.55</td>
<td>0.45</td>
</tr>
<tr>
<td>$P = 5.5 \text{ MPa}$</td>
<td>$u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$</td>
<td>0.335</td>
<td>1.05</td>
<td>0.405</td>
<td>1.95</td>
<td>0.40</td>
<td>0.03</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$T = 323 \text{ K}$</td>
<td>$u_{\text{CGSS}}^{\text{wall-CO}_2}$</td>
<td>0.335</td>
<td>0.45</td>
<td>0.405</td>
<td>0.55</td>
<td>0.365</td>
<td>0.05</td>
<td>0.55</td>
<td>0.45</td>
</tr>
<tr>
<td>$P = 1.01 \text{ MPa}$</td>
<td>$u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$</td>
<td>0.335</td>
<td>1.15</td>
<td>0.405</td>
<td>1.65</td>
<td>0.40</td>
<td>0.03</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>

TABLE I. Parameters of CGSS wall-fluid and fluid-fluid interaction potentials.
III. QUASI-CONTINUUM POTENTIAL MODELS FOR CARBON DIOXIDE

In quasi-continuum potential models, the potential of mean force, \( U(r) \), that acts on a particle placed at position \( r \) is computed by applying the continuum approximation to the discrete summation expression for the total interaction potential experienced by the particle in the molecular representation,\(^{15} \) i.e.,

\[
U(r) = \sum_{i=1}^{N} u^{AA}(|r - r_i|),
\]

\[
\approx \int_{\Omega} u^{AA}(|r - r'|) \rho(r') \, dr',
\]

Here, \( u^{AA} \) is the inter-atomic potential that describes the interaction between two atoms, \( N \) is the number of atoms which lie within the cutoff sphere around the position \( r \), \( r_i \) is the location of atom \( i \), \( \rho \) is the density of the atoms in the volume element \( dr' \), and \( \Omega \) is the volume circumscribed by the cutoff sphere. The inter-atomic potential, \( u^{AA}(r) \), and the density distribution, \( \rho(r) \), are the inputs required to develop the quasi-continuum potentials. For simple LJ type spherical molecules, \( u^{AA} \) is typically a 12–6 LJ interaction potential. For polyatomic molecules, the molecular interactions are typically described through the interaction potentials that define the interactions between the constituent atoms and depend on the internal coordinates of each molecule. To develop the quasi-continuum potentials for polyatomic molecules, we first develop an effective or coarse-grained pair-potential that describes the interaction between two molecules and then use it in the continuum approximation (Eq. (16)) to compute the PMF. We use \( u^{CGSS}_{\text{wall-CO}_2} \) and \( u^{CGSS}_{\text{CO}_2-CO}_2 \) to develop the quasi-continuum potential models for confined carbon dioxide, i.e.,

\[
U_{\text{wall-CO}_2}(r) \approx \int_{\Omega} u^{CGSS}_{\text{wall-CO}_2}(|r - r'|) \rho_{\text{wall}}(r') \, dr',
\]

\[
U_{\text{CO}_2-CO}_2(r) \approx \int_{\Omega} u^{CGSS}_{\text{CO}_2-CO}_2(|r - r'|) \rho_{\text{CO}_2}(r') \, dr',
\]

\[
U(r) = U_{\text{wall-CO}_2}(r) + U_{\text{CO}_2-CO}_2(r).
\]

Here, \( \rho_{\text{wall}} \) and \( \rho_{\text{CO}_2} \) (the unknown concentration \( c \) in the NP equation) are the wall and the fluid density, respectively.
$U_{\text{wall-CO}_2}(r)$ and $U_{\text{CO}_2-CO}_2(r)$ are the wall-fluid and the fluid-fluid PMF, respectively. Assuming the wall to be a continuum of uniform density, $(\rho_{\text{wall}} = \text{constant})$, the wall-fluid PMF given by Eq. (17) can be computed straightforwardly. For confined systems, the computation of the fluid-fluid PMF (Eq. (18)) can be complicated and needs to be performed carefully. Due to the inhomogeneous nature of the fluid density, $\rho_{\text{CO}_2}$, and the highly repulsive nature of the intermolecular potential, $U_{\text{CGSS-CO}_2}$, the evaluation of the integral given by Eq. (18) can lead to numerical singularity. In the region next to the walls, where $\rho_{\text{CO}_2}(r') \approx 0$, the integrand $U_{\text{CGSS-CO}_2}(r') \times \rho_{\text{CO}_2}(r')$ in Eq. (18) should $\to 0$. However, because of the very strong repulsive nature of $U_{\text{CGSS-CO}_2}$ in the region $|r - r'| < \sigma_1$, this product can diverge even when $\rho_{\text{CO}_2}(r') \approx 0$ ($U_{\text{CGSS-CO}_2}(\sim 10^9) \times \rho_{\text{CO}_2}(\sim 10^{-3})$). To avoid this problem of numerical singularity we introduce a truncated softer repulsive core potential, $u_{\text{soft-CO}_2-CO}_2(r)$ (see Fig. 2(b)), to replace $U_{\text{CGSS-CO}_2}(r)$ and compute the fluid-fluid PMF as

$$U_{\text{CO}_2-CO}_2(r) \approx \int_{\Omega} u_{\text{soft-CO}_2-CO}_2(|r - r'|) \rho_{\text{CO}_2}(r') \, dr', \quad (20)$$

where $u_{\text{soft-CO}_2-CO}_2(r)$ is defined as

$$u_{\text{soft-CO}_2-CO}_2(r) = \begin{cases} 0 & r \leq R_{\text{crit}} \\ b_0 + b_1 r + b_2 r^2 & R_{\text{crit}} < r \leq R_{\text{min}}, \\ u_{\text{CGSS-CO}_2}(r) & r > R_{\text{min}} \end{cases} \quad (21)$$

$R_{\text{min}}$ and $R_{\text{crit}}$ are two new coarse-graining parameters, which define the softer repulsive region and the zero potential core, respectively. We use a second-order polynomial function to model the softer repulsive interactions. The coefficients $b_0$, $b_1$, and $b_2$ are calculated to ensure the continuity of the softer potential and its first and second derivative at $R_{\text{min}}$. The functional form of the softer repulsive core is an ansatz and lacks any fundamental derivation. This issue of numerical singularity and the idea of using a truncated softer repulsive core potential as a possible way to avoid it are discussed in our earlier publication (Singh and Aluru[16] on EQT for confined simple LJ type fluids. The parameters $R_{\text{min}}$ and $R_{\text{crit}}$ are chosen such that the total PMF profile, $U(r)$, of the confined fluid obtained from the quasi-continuum potentials matches with the total PMF profile, $U^{\text{AA}}(r)$, obtained from the AA-MD simulation. The procedure for parameterizing $u_{\text{soft-CO}_2-CO}_2$ is summarized in Algorithm II. Once the quasi-continuum potentials are developed for a particular thermodynamic state, they can be used in EQT to very quickly obtain the concentration and potential profiles of carbon dioxide inside different size confinements. Since, the fluid-fluid PMF, $U_{\text{CO}_2-CO}_2$ (Eq. (20)), is a function of the unknown fluid density, $\rho_{\text{CO}_2}$, the concentration ($c$) and the potential ($U$) profiles in EQT are computed by solving the NP equation (Eq. (1)) iteratively, until a self-consistent solution is obtained (see Ref. 15 for implementation details).

Figure 5 shows the comparison of the COM density and potential profiles obtained by using the quasi-continuum models in EQT (solid line) with the AA-MD simulation results (open circle) for supercritical carbon dioxide ($T = 348$ K and $P = 9.05$ MPa) confined inside a 2.232 nm wide graphite slit pore. The parameters used in $U_{\text{CGSS-\text{wall-CO}_2}}$ and $U_{\text{CGSS-CO}_2}^{(\text{open circle})}$ for this thermodynamic state are reported in Table I. Parameters $R_{\text{min}}$ and $R_{\text{crit}}$ are obtained using Algorithm II, and are reported in Table II. Also shown in Fig. 5 are the COM density and potential profiles for carbon dioxide confined inside a 1.488 nm wide graphite slit pore as obtained from EQT. It can be observed that the results obtained from EQT are in good agreement with those obtained from AA-MD simulations. We note that even though we have discussed the quasi-continuum potential formulation for slit pores, the same approach can be straightforwardly applied to other slit-like geometries, where the total potential varies along just one dimension. In addition, for geometries where the total potential varies in two or three dimensions, the EQT framework can be extended by considering a multi-dimensional form of Eq. (1).

### IV. SIMULATION DETAILS

All MD simulations are performed in the NVT ensemble using the simulation package GROMACS 3.3.1.[20] In AA-MD simulations, carbon dioxide is modeled as a linear (O–C–O angle = 180°), rigid (fixed bond lengths) 3-site LJ molecule with partial charges. The parameters are taken from the model proposed by Zhang and Duan[9] with the values $\sigma_{\text{O-O}} = 0.30$ nm, $\epsilon_{\text{O-O}} = 0.68724$ kJ/mol, $\sigma_{\text{C-C}} = 0.27918$ nm, $\epsilon_{\text{C-C}} = 0.23983$ kJ/mol, and point charges of $q_{\text{O}} = -0.2944$ and $q_{\text{C}} = 0.5888$. The O–O bond length is 0.2326 nm, and C–O bond length is 0.1163 nm. To properly handle the 180° angle constraint in GROMACS, two dummy mass particles are used. The dummy mass particles are constructed such that their mass and moment of inertia is identical to that of the CO$_2$ molecule. The position of the massless C and O atoms is constructed from the position of the dummy mass particles using the concept of virtual interaction-sites.[20] Electrostatic interactions are computed using the particle mesh Ewald (PME) method[22,23] with Fourier spacing of 0.15 nm. The LINCS (Linear Constraint Solver) algorithm is used to maintain the shape of the molecule.

### TABLE II. Softer repulsive core parameters.

<table>
<thead>
<tr>
<th>Thermodynamic state</th>
<th>$R_{\text{crit}}$ (nm)</th>
<th>$R_{\text{min}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 323 K, P = 10.1 MPa</td>
<td>0.174</td>
<td>0.364</td>
</tr>
<tr>
<td>T = 323 K, P = 1.01 MPa</td>
<td>0.201</td>
<td>0.364</td>
</tr>
<tr>
<td>T = 348 K, P = 9.05 MPa</td>
<td>0.174</td>
<td>0.362</td>
</tr>
<tr>
<td>T = 308 K, P = 5.50 MPa</td>
<td>0.164</td>
<td>0.365</td>
</tr>
</tbody>
</table>
graphite wall is modeled as four graphene layers with lateral dimensions $4.550 \times 4.331$ nm$^2$ ($\rho_{\text{wall}} \approx 35$ atoms/nm$^2$) and an inter-layer spacing of 0.335 nm. The interaction parameters for graphite wall atoms have the values $\sigma_{\text{w-w}} = 0.34$ nm, $\epsilon_{\text{w-w}} = 0.23279$ kJ/mol.$^{13, 14}$ The Lorentz-Berthelot rules are used to estimate the cross interaction parameters.

In CG-MD simulations, CO$_2$ is represented as a single-site molecule placed at its COM position. The wall-fluid and fluid-fluid interactions are defined by $u_{\text{CGSS}}^{\text{wall-CO}_2}$ and $u_{\text{CGSS}}^{\text{CO}_2-\text{CO}_2}$, respectively, and are specified using the table option in the mdrun program of GROMACS. For both AA-MD and CG-MD simulations, Nosé-Hoover thermostat$^{24}$ with a time constant of 0.1 ps is used to maintain the temperature of the fluid. LJ cutoff distance is set to 1.2 nm and a time step of 1 fs is used to simulate the system. For a given thermodynamic state, MD simulation of the fluid in different size slit pores requires the density of the fluid within the pore as an input. The density of carbon dioxide inside different width graphite slit pores is obtained from the adsorption isotherms reported by Zhou and Wang$^{17}$ and Samios et al.$^{18}$ In EQT, the wall-fluid PMF, $U_{\text{wall-CO}_2}$ (Eq. (17)), is computed by assuming the graphite surface as a continuum graphene layer with $\rho_{\text{wall}} = 35$ atoms/nm$^2$ and an inter-layer spacing of 0.335 nm. This coarse-graining strategy of ignoring the discrete position of atoms in each layer works fine for flat surfaces, but might be inappropriate for disordered or heterogeneous surfaces.

The strategies to develop quasi-continuum wall-fluid potential models for heterogeneous and patterned surfaces are discussed in Refs. 25–29. Fluid-fluid PMF, $U_{\text{CO}_2-\text{CO}_2}$, is computed using Eq. (20). 1D NP equation (Eq. (1)) is solved using the finite volume method.$^{15}$

V. RESULTS

A. COM density profiles from EQT

We use quasi-continuum potentials in EQT to predict the COM density profile of CO$_2$ confined inside different width (1.05 to 3.72 nm) graphite slit pores. Figure 6 shows the comparison of the COM density profiles at a high and a low pressure confinement state ($P = 10.1$ MPa and $1.01$ MPa; $T = 323$ K). For both these states the potentials are parameterized using the AA-MD data of $H = 2.232$ nm wide graphite slit. The parameters are reported in Tables I and II. It can be observed that the density profiles obtained from EQT (solid line) match well with those obtained from AA-MD simulations (open circle). For bigger pores ($H = 3.72$ and 2.976 nm), the developed potentials capture both the density layering in the interfacial region and the bulk like behavior in the central region of the pores. For smaller pores ($H = 1.488$ and 1.116 nm), confinement makes the density inhomogeneous across the entire length of the pore, which is also captured well with these potentials. At low pressure (low density) confinements, most of the fluid confinement occurs near the wall.
Also, the density layer in the interfacial region does not split into two sub-layers and resembles like that of confined simple LJ type fluids. Figure 7 shows the COM density profiles at two different supercritical temperature states ($T = 348$ K, $P = 9.05$ MPa and $T = 308$ K, $P = 5.5$ MPa) as obtained from EQT. For $T = 348$ K state, the potentials are parameterized using the AA-MD data of $H = 2.232$ nm wide slit, while for $T = 308$ K state, AA-MD data of $H = 1.850$ nm wide slit is used to parameterize the potentials. The parameters are reported in Tables I and II. Again, the results obtained from

![Graph showing COM density profile of carbon dioxide confined inside different width graphite slit pores at two different supercritical temperature states. Solid line represents the results from EQT and open circle are the AA-MD results. $c_{\text{avg}}$ is reported in units of molecules/nm$^3$.](image_url)
EQT are in good agreement with those obtained from AA-MD simulations. The general structural behavior at these two states looks quite similar to each other.

**B. COM density profiles from CG-MD simulations**

The CGSS wall-CO$_2$ and CO$_2$-CO$_2$ interaction potentials developed in this work are also used to perform CG-MD simulations. The objective of performing CG-MD simulations is to check their performance in a particle based CG simulation method. Figure 8 shows the comparison of the density profiles obtained from the CG-MD simulations (solid line) with the AA-MD (open circle) results for the four thermodynamic states considered in this work. It can be observed that the results obtained from CG-MD simulations are in reasonable agreement with those obtained from AA-MD simulations.
VI. CONCLUSIONS

In this work, CGSS wall-CO$_2$ and CO$_2$-CO$_2$ interaction potential models are proposed to study the structure of carbon dioxide in confined environments. The CGSS potentials are used to develop quasi-continuum potential models, which are used in EQT to study the equilibrium structure of carbon dioxide confined in different size graphite slit pores. The results obtained from EQT are found to be in good agreement with those obtained from AA-MD simulations. For a given thermodynamic state, the development of the quasi-continuum potentials require just one AA-MD simulation. Once developed, they can be used in EQT to very quickly predict the COM density and potential profiles of carbon dioxide in different size confinements. Further, the CGSS potentials are also used to perform CG-MD simulations to predict the COM density profile of carbon dioxide confined inside different size slit pores. The results obtained from CG-MD simulations also match reasonably well with AA-MD simulations. The transferability of the functional form of CGSS potentials is tested in the temperature and pressure range of 308–348 K and 1–10 MPa, respectively. In this range of practical interest, the potentials reproduce the wall-fluid and the fluid-fluid PMF profiles in reasonable agreement with those obtained from AA-MD simulations.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (NSF) under Grants 0328162 (nano-CEMMS, UIUC), 0852657 and 0915718. T. Sanghi acknowledges the department of Mechanical Science and Engineering, UIUC, for Eugene and Lina Abraham Fellowship. T. Sanghi also wishes to thank Sikandar Mashayak and Joonho Lee for helpful discussions.

3F. Rigas, J. Colloid Interface Sci. 224, 224 (2000).

FIG. 9. Comparison of the COM density profile inside H = 0.60 nm (left) and H = 0.744 nm (right) slit pores as obtained from CG-MD simulations (broken line) and EQT (solid line) with those obtained from AA-MD simulations (open circle).

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