



Dual Control Cell Reaction Ensemble Molecular Dynamics: A Method for Simulations of Reactions and Adsorption in Porous Materials

by Martin Lísal, John K. Brennan, William R. Smith, and Flor R. Siperstein

ARL-RP-146

September 2006

A reprint from the *Journal of Chemical Physics*, vol. 121, no. 10, pp. 4901–4912, 8 September 2004.

Reprinted with permission from the *Journal of Chemical Physics*.
Copyright 2004, the American Institute of Physics.

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5066

ARL-RP-146

September 2006

Dual Control Cell Reaction Ensemble Molecular Dynamics: A Method for Simulations of Reactions and Adsorption in Porous Materials

Martin Lísal

**Institute of Chemical Process Fundamentals and
J. E. Purkyně University, Czech Republic**

John K. Brennan

Weapons and Materials Research Directorate, ARL

William R. Smith

**University of Ontario Institute of Technology,
Canada**

Flor R. Siperstein

Universitat Rovira i Vergili, Spain

A reprint from the Journal of Chemical Physics, vol. 121, no. 10, pp. 4901–4912, 8 September 2004.

*Reprinted with permission from the Journal of Chemical Physics.
Copyright 2004, the American Institute of Physics.*

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) September 2006		2. REPORT TYPE Reprint		3. DATES COVERED (From - To) January 2004–August 2004	
4. TITLE AND SUBTITLE Dual Control Cell Reaction Ensemble Molecular Dynamics: A Method for Simulations of Reactions and Adsorption in Porous Materials				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Martin Lísal,* John K. Brennan, William R. Smith, [†] and Flor R. Siperstein [‡]				5d. PROJECT NUMBER H4311	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRD-ARL-WM-BD Aberdeen Proving Ground, MD 21005-5066				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-RP-146	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES *E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague, Czech Republic and Department of Physics, J. E. Purkyně University, 400 96 Ustí n. Lab., Czech Republic [†] Faculty of Science, University of Ontario Institute of Technology, 2000 Simcoe St. N., Oshawa ON L1H7K4, Canada [‡] Department d'Enginyeria Química, ETSEQ, Universitat Rovira i Vergili, Avinguda dels Països Catalans, 26. 43007 Tarragona, Spain A reprint from the <i>Journal of Chemical Physics</i> , vol. 121, no. 10, pp. 4901–4912, 8 September 2004.					
14. ABSTRACT We present a simulation tool to study fluid mixtures that are simultaneously chemically reacting and adsorbing in a porous material. The method is a combination of the reaction ensemble Monte Carlo method and the dual control volume grand canonical molecular dynamics technique. The method, termed the dual control cell reaction ensemble molecular dynamics method, allows for the calculation of both equilibrium and nonequilibrium transport properties in porous materials such as diffusion coefficients, permeability, and mass flux. Control cells, which are in direct physical contact with the porous solid, are used to maintain the desired reaction and flow conditions for the system. The simulation setup closely mimics an actual experimental system in which the thermodynamic and flow parameters are precisely controlled. We present an application of the method to the dry reforming of methane reaction within a nanoscale reactor model in the presence of a semipermeable membrane that was modeled as a porous material similar to silicalite. We studied the effects of the membrane structure and porosity on the reaction species permeability by considering three different membrane models. We also studied the effects of an imposed pressure gradient across the membrane on the mass flux of the reaction species. Conversion of syngas (H ₂ /CO) increased significantly in all the nanoscale membrane reactor models considered. A brief discussion of further potential applications is also presented.					
15. SUBJECT TERMS molecular simulation, Monte Carlo, reaction ensemble					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON John K. Brennan
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (Include area code) 410-306-0678

Dual control cell reaction ensemble molecular dynamics: A method for simulations of reactions and adsorption in porous materials

Martin Lísal^{a)}

E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchbát, Czech Republic and Department of Physics, J. E. Purkyně University, 400 96 Ustí n. Lab., Czech Republic

John K. Brennan

U.S. Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, Maryland 21005-5066

William R. Smith

Faculty of Science, University of Ontario Institute of Technology, 2000 Simcoe St. N., Oshawa ON L1H7K4, Canada

Flor R. Siperstein

Departament d'Enginyeria Química, ETSEQ, Universitat Rovira i Virgili, Avinguda dels Països Catalans, 26. 43007 Tarragona, Spain

(Received 16 March 2004; accepted 21 June 2004)

We present a simulation tool to study fluid mixtures that are simultaneously chemically reacting and adsorbing in a porous material. The method is a combination of the reaction ensemble Monte Carlo method and the dual control volume grand canonical molecular dynamics technique. The method, termed the dual control cell reaction ensemble molecular dynamics method, allows for the calculation of both equilibrium and nonequilibrium transport properties in porous materials such as diffusion coefficients, permeability, and mass flux. Control cells, which are in direct physical contact with the porous solid, are used to maintain the desired reaction and flow conditions for the system. The simulation setup closely mimics an actual experimental system in which the thermodynamic and flow parameters are precisely controlled. We present an application of the method to the dry reforming of methane reaction within a nanoscale reactor model in the presence of a semipermeable membrane that was modeled as a porous material similar to silicalite. We studied the effects of the membrane structure and porosity on the reaction species permeability by considering three different membrane models. We also studied the effects of an imposed pressure gradient across the membrane on the mass flux of the reaction species. Conversion of syngas (H_2/CO) increased significantly in all the nanoscale membrane reactor models considered. A brief discussion of further potential applications is also presented. © 2004 American Institute of Physics. [DOI: 10.1063/1.1782031]

I. INTRODUCTION

With the rapid growth of nanotechnology and the invention of various nanomaterials, some of these materials have been proposed as vehicles for nanochemical devices such as nanoscale reactors and nanoscale membrane reactors.¹ However, development of these applications is impossible without fundamental knowledge of reaction, adsorption, and transport mechanisms in the nanoporous materials.

It is well established that confinement brings about drastic changes in the thermodynamics properties of fluids such as narrowing of the coexistence curve, lowering of the pore critical temperature, or increasing the average pore densities; for a comprehensive review see Ref. 2. Confinement also influences chemical reaction equilibrium. For example, gen-

erally the pore phase has a higher density than the corresponding bulk phase; this results in an increase in yield for reactions in which there is a decrease in the total number of moles (Le Chatellier's principle). Further, some components of the reaction mixture are selectively adsorbed on the solid surfaces, subsequently affecting the reaction equilibrium. Finally, molecular orientations can be strongly influenced by proximity to a solid surface which also can shift the reaction equilibrium from the bulk phase equilibrium. The effects of confinement on reaction equilibria were already studied by Turner *et al.*³⁻⁵ for several realistic, reversible reactions in carbon micropores and carbon nanotubes, and by Borówko *et al.*^{6,7} for model, reversible reactions in slitlike pores.

These authors employed the reaction ensemble Monte Carlo (REMC) simulation technique⁸⁻¹⁰ that enables us to directly simulate equilibrium properties of chemically reacting systems. The method requires only a knowledge of the reaction species intermolecular potentials and their ideal-gas properties, in addition to specification of the system stoichi-

^{a)}Author to whom correspondence should be addressed. Present address: E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague 6-Suchbát, Czech Republic.

ometry and thermodynamic constraints. Recently, we proposed a combination of the REMC method with the molecular dynamics (MD) technique.¹¹ The method, termed the reaction ensemble molecular dynamics (RxMD) method, uses a combination of stochastic and dynamic simulation steps, allowing for the simulation of both thermodynamic and transport properties. The method couples a MD system (dynamic cell) to a reaction mixture reservoir (control cell) that is formulated upon the REMC method. Thermodynamic and transport properties are calculated in the dynamic cell by using a canonical MD simulation method. The RxMD method is analogous to the grand canonical molecular dynamics (GCMD) technique of Papadopolou *et al.*¹² The accuracy and stability of the RxMD method was assessed by considering the ammonia synthesis reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

Confinement also influences the transport properties of fluid particles inside the nanoporous materials. Physical space restrictions based on the fluid particle size or geometry may limit flow of particles through particular pores in the material. Furthermore, attraction of the pore surface, i.e., physisorption may play a critical role. Even further complicating the matters, fluid particles may chemisorb. In addition to phenomena occurring between fluid particles and the pore surface, behavior in the porous material becomes increasingly more complex if chemical reactions occur between fluid particles.

Confinement contributes significantly to the thermodynamic and transport properties if reactions and separation occur simultaneously in the nanoporous materials. Consider, for example, two voids in a nanoporous material separated by a semipermeable membrane with the elementary reversible reaction



occurring in one void only. If the membrane is permeable to product *D* only and the partial pressure of *D* on the permeate side of the membrane is lower than the partial pressure of *D* on the reaction side of the membrane then the separation process produces a flow of product *D* across the membrane. The removal of *D* from the “reaction” void via the separation function of the membrane has the following effects on the reaction shown in Eq. (1): (i) the reaction equilibrium condition is shifted to the right resulting in a higher conversion of reactants *A* and *B* to products *C* and *D*; (ii) if there is an undesirable side reaction, e.g., that fouls a catalyst by a side product, such as



occurring in the reaction void, then the separation of product *D* from the reaction mixture reduces the amount of reactant *B* to the side reaction, increasing the selectivity of conversion to product *C* (or *D*).¹³

In this work, we propose a nonequilibrium MD method for the simulation of combined reaction and adsorption mechanisms in porous materials. This method is a combination of the REMC and RxMD methods, and the dual control volume GCMD (DCV-GCMD) technique. The REMC and RxMD methods predict the physical effects on chemical re-

action equilibria from such influences as solvation and confinement. In addition, the RxMD method predicts the effects of nonideal environments on the molecular transport properties of chemically reacting mixtures. The DCV-GCMD method was independently proposed by Heffelfinger and van Swol,¹⁴ and MacElroy,¹⁵ and was extensively employed for studies of transport phenomena in confined systems; see, e.g., Refs. 16 and 17, and references therein.

We term the nonequilibrium simulation method the dual control cell reaction ensemble molecular dynamics (DCC-RxMD) method. The DCC-RxMD method allows for the simulation of the thermodynamic and transport properties of fluids in porous materials where reaction and adsorption is occurring simultaneously. Fluid particles move through the simulation cell via MD,¹⁸ chemical reactions occur via the REMC method, and fluid transport (occurring as a result of an imposed pressure gradient between adjacent pores) via the grand canonical Monte Carlo (GCMC) method.¹⁹

We apply the DCC-RxMD method to study reactions and separations in a model of a nanoscale membrane reactor for dry reforming of methane. Dry reforming of methane is an important industrial process for producing syngas (H_2/CO) that utilizes membrane technology.²⁰ We examine the effects of the membrane structure and porosity on the reaction species permeability by considering three different membrane models. We also examine the effects of an imposed pressure gradient across the membrane on the mass flux of the reaction species and reaction conversion.

The paper is organized as follows: Derivation and general computational considerations of the DCC-RxMD methodology are presented in Sec. II. Section III describes an illustrative application of the DCC-RxMD method for simulation of a multicomponent system in which both a chemical reaction (dry reforming of methane) and physisorption is occurring within a nanoporous solid. In addition, the technical details of this application of the DCC-RxMD methodology are given. Section IV presents and discusses DCC-RxMD results together with DCV-GCMD simulations for both the pure fluids and equimolar mixtures of the reaction components (CH_4 , CO_2 , H_2 , CO). Section V contains our conclusions including a brief discussion of further potential applications of the DCC-RxMD method.

II. SIMULATION METHODOLOGY

A molecular simulation method to study reactions and adsorption in porous materials is presented. The method uses a combination of stochastic and dynamic simulation steps, allowing for the simulation of both thermodynamic and transport properties. The method couples a MD system (dynamic cell) to reaction and nonreaction mixture reservoirs (control cells) that are formulated upon the REMC method^{8–10} and GCMC method,¹⁹ hence the term dual control cell reaction ensemble molecular dynamics (DCC-RxMD) method. The control cells are in direct contact with the dynamic cell and the particles are able to move freely between the cells. Transport properties are calculated in the dynamic cell by using a MD simulation method.¹⁸ REMC forward and reverse reaction steps, and GCMC particle insertion and deletion steps are performed in the control cells

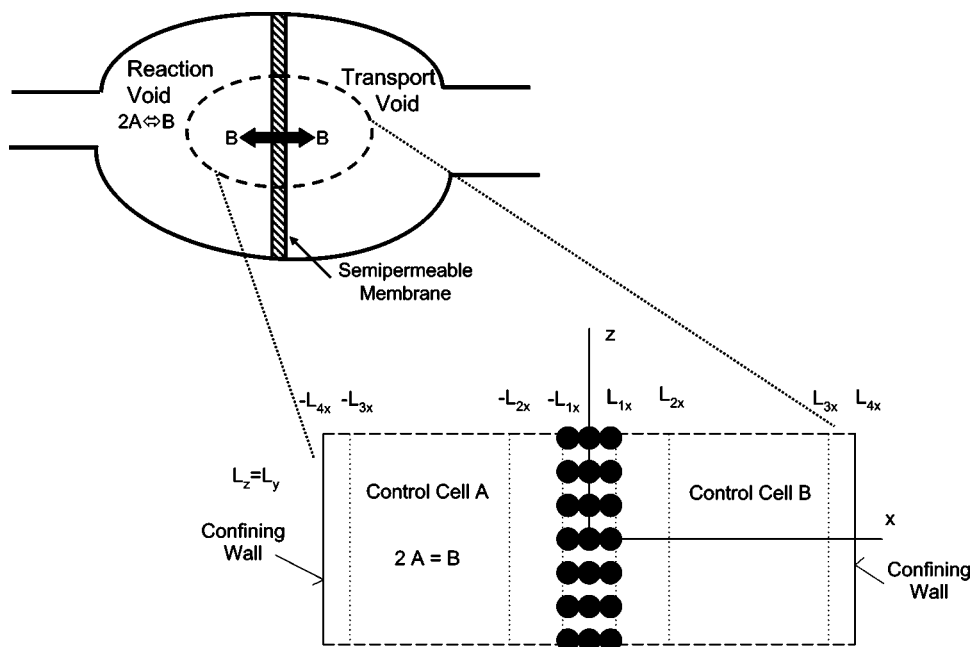


FIG. 1. Schematic of a nanoscale membrane reactor model made up of a reaction void and a transport void separated by a semipermeable membrane. A model reaction $2A \rightleftharpoons B$ takes place in the reaction void while component B is separated via the semipermeable membrane. Enlargement shows schematic of the corresponding DCC-RxMD simulation setup. Periodic boundary conditions, applied in both the y and z directions, are omitted in the x direction due to the presence of repulsive confining walls (in the yz plane) at each end of the simulation setup.

only, while MD steps are performed in both the dynamic cell and the control cells. The control cells, which act as sink and source reservoirs, are maintained at explicitly defined and controlled gradient conditions, e.g., a pressure gradient. The DCC-RxMD method is analogous to the DCV-GCMD method;^{14,15} all of which simulate conditions that directly relate to real, open systems. Computational details will be addressed below but first we illustrate the overall setup of the method.

Consider a nanoporous material containing a system of “nanomembrane reactors.” Each nanomembrane reactor is made up of two adjacent voids separated by a semipermeable membrane. One of the voids acts as a “nanoreactor” in which, for example, the model reaction



is occurring. We term this void the *reaction* void. The accompanying void in the nanomembrane reactor, termed the *transport* void, maintains a pressure gradient across the membrane. We further assume that the membrane separating the reaction and transport voids is not permeable to all molecular components. For example, in the model system of Eq. (3), suppose the membrane is permeable to component B only. For such a case, a difference in the partial pressures of component B in the reaction and transport voids results in a flux of component B through the membrane. A schematic of the nanomembrane reactor model made up of the reaction and transport voids separated by a semipermeable membrane is presented in Fig. 1. The nanomembrane reactor model is analogous to the slitpore model²¹ which assumes that the nanomembrane reactor model is taken as representative of all nanomembrane reactors in the porous material. The effect of pore connectivity can be readily involved by considering a combination of connected nanomembrane reactor models.

To mimic reaction and adsorption mechanisms in such a nanoscale membrane reactor model, we consider a DCC-RxMD simulation box as shown in the enlargement of Fig. 1.

A membrane of thickness $\delta = 2L_{1x}$ is placed at the center of the simulation box. The left-hand side of the simulation box (from $-L_{1x}$ to $-L_{4x}$) with control cell (CC) A (from $-L_{2x}$ to $-L_{3x}$) corresponds to a reaction void while the right-hand side of the simulation box (from L_{1x} to L_{4x}) with CC B (from L_{2x} to L_{3x}) corresponds to a transport void. Box lengths in the y and z directions are denoted by L_y and L_z , respectively. For simplicity, we considered that both CC A and CC B are of the same size and are positioned symmetrically with respect to the yz plane at $x = 0$. We impose periodic boundary conditions in both the y and z directions since we assume that the sizes of the reaction and transport voids in these directions are much larger than the membrane thickness. To limit the size of the simulation setup in the x direction, repulsive confining walls are placed at the end of the simulation box. The size of the simulation box in the x direction must be sufficiently large to ensure that these confining-wall boundaries have negligible effect on the calculated fluid properties. The alternative to including confining-wall boundaries is to allow the fluid particles to leave the simulation box at the boundaries. Use of either the confining-wall boundaries or open-end boundaries give the same simulation results.^{15,22} An alternative scenario is possible here. For example, one can consider a DCC-RxMD simulation box with two confining walls located in the z direction at a distance L_z apart without confining walls in the x direction.²² In this scenario, confinement effects in the z direction are also considered important.

In either scenario, the DCC-RxMD simulation proceeds as follows. After n_{MD} MD steps, the system is frozen, i.e., particle positions are held fixed, and we perform n_{REMC} forward and reverse reaction steps in CC A, and n_{GCMC} particle creation and destruction steps in CC B. Both the REMC and GCMC algorithms require insertion of particles into the CCs. The velocities for such particles are assigned from a Maxwell-Boltzmann distribution corresponding to the speci-

fied system temperature.^{11,12} Values of n_{MD} , n_{REMC} , and n_{GCMC} must be chosen appropriately to maintain reaction equilibrium in CC A, constant chemical potentials in CC B, and reasonable transport rates at the boundaries between the CCs and the membrane region (the dynamic cell).

A. Isothermal molecular dynamics

Trajectories of fluid particles within the entire DCC-RxMD simulation volume are generated by the MD simulation method.¹⁸ The imposed pressure gradient across the membrane (a difference between pressures in CC A and CC B) produces heat that must be removed to maintain isothermal transport. Removal of the heat can be achieved by keeping the kinetic energy of the system E_k constant during MD steps.²³ E_k is defined in terms of $\Delta \mathbf{p}_{i,l} = \mathbf{p}_{i,l} - \mathbf{p}_l$, the relative momenta of particles with respect to the streaming momentum per particle for each of components l , $\mathbf{p}_l$, evaluated as

$$\mathbf{p}_l = \frac{1}{N_l} \sum_{i=1}^{N_l} \mathbf{p}_{i,l}. \quad (4)$$

In Eq. (4), N_l is the number of particles of component l in the system and $\mathbf{p}_{i,l}$ is the momentum of particle i for component l . The kinetic energy constraint for the system will be satisfied²⁴ if

$$\frac{dE_k}{dt} = \frac{1}{2} \frac{d}{dt} \left[\sum_{l=1}^c \frac{1}{m_l} \sum_{i=1}^{N_l} (\Delta \mathbf{p}_{i,l})^2 \right] = 0, \quad (5)$$

where t is the time, m_l is the mass of component l , and c is the total number of components in the system. A set of equations of motion for the MD subject to the kinetic energy constraint given by Eq. (5) is²⁵

$$\frac{d\mathbf{r}_{i,l}}{dt} = \frac{\mathbf{p}_{i,l}}{m_l}, \quad (6)$$

$$\frac{d\mathbf{p}_{i,l}}{dt} = \mathbf{f}_{i,l} - \alpha(\Delta \mathbf{p}_{i,l}), \quad (7)$$

where $\mathbf{r}_{i,l}$ is the position of particle i for component l and $\mathbf{f}_{i,l}$ is the force on such a particle. α is computed from Eq. (5) as²⁶

$$\alpha = \frac{\sum_{l=1}^c \frac{1}{m_l} \sum_{i=1}^{N_l} (\mathbf{f}_{i,l} \cdot \Delta \mathbf{p}_{i,l})}{\sum_{l=1}^c \frac{1}{m_l} \sum_{i=1}^{N_l} (\Delta \mathbf{p}_{i,l} \cdot \Delta \mathbf{p}_{i,l})} \quad (8)$$

$$= \frac{\frac{1}{2} \sum_{l=1}^c \frac{1}{m_l} \sum_{i=1}^{N_l} (\mathbf{f}_{i,l} \cdot \Delta \mathbf{p}_{i,l})}{E_k}. \quad (9)$$

The equations of motion for the isothermal MD method, Eqs. (6) and (7), were solved by the “leap-frog” version of the Verlet algorithm.²⁶ The algorithm starts with Eq. (7) by evaluating the unconstrained relative momenta $\Delta \mathbf{p}_{i,l}^{un}$ at time t ,

$$\Delta \mathbf{p}_{i,l}^{un}(t) = \Delta \mathbf{p}_{i,l}(t - \Delta t/2) + \frac{\Delta t}{2} [\mathbf{f}_{i,l}(t) - \mathbf{f}_l(t)], \quad (10)$$

where Δt is the time step and

$$\mathbf{f}_l = \frac{1}{N_l} \sum_{i=1}^{N_l} \mathbf{f}_{i,l}. \quad (11)$$

$\Delta \mathbf{p}_{i,l}^{un}(t)$ is then used to compute an instantaneous temperature of the system $\mathcal{T}(t)$ from the relation

$$\frac{F}{2} k_B \mathcal{T}(t) = \frac{1}{2} \sum_{l=1}^c \frac{1}{m_l} \sum_{i=1}^{N_l} (\Delta \mathbf{p}_{i,l}^{un})^2, \quad (12)$$

where $F = 3(\sum_{l=1}^c N_l) - 1$ is the total number of degrees of freedom for the system and k_B is the Boltzmann's constant. $\mathcal{T}(t)$ and the specified system temperature T are used to evaluate the constant β defined as

$$\beta = \sqrt{\frac{T}{\mathcal{T}(t)}}, \quad (13)$$

where β is related to the constant α [defined by Eqs. (8) and (9)] via

$$\beta = \frac{1}{1 + \alpha(\Delta t/2)}. \quad (14)$$

Having determined β , we are able to obtain $\mathbf{p}_{i,l}$ at time $t + \Delta t/2$ as

$$\mathbf{p}_{i,l}(t + \Delta t/2) = (2\beta - 1)\mathbf{p}_{i,l}(t - \Delta t/2) + 2(\beta - 1)\mathbf{p}_l(t - \Delta t/2) + \Delta t[\beta \mathbf{f}_{i,l}(t) + (1 - \beta)\mathbf{f}_l(t)]. \quad (15)$$

Finally, $\mathbf{r}_{i,l}$ at time $t + \Delta t$ is obtained from Eq. (6) as

$$\mathbf{r}_{i,l}(t + \Delta t) = \mathbf{r}_{i,l}(t) + \Delta t \frac{\mathbf{p}_{i,l}(t + \Delta t/2)}{m_l}. \quad (16)$$

B. Reaction ensemble Monte Carlo

The REMC method^{8–10} is a powerful simulation tool for studying chemically reacting mixtures. The method only requires inputting the intermolecular potentials and the ideal-gas properties for the reaction species that are present. Most notably, the method does not require a reactive-type potential that mimics bond breakage and formation.^{27,28} The REMC method predicts the shift in equilibria of an ideal-gas phase reaction due to nonideal conditions such as high temperature and high pressure as well as nonideal surrounding environments such as solvents and pore walls. Reactions are simulated by performing forward and reverse reaction steps according to the REMC algorithm which guarantees that the reaction equilibrium criteria for a set of R linearly, independent chemical reactions,

$$\sum_{i=1}^c \nu_{ji} \mu_i = 0, \quad j = 1, 2, \dots, R, \quad (17)$$

are established.²⁹ In Eq. (17), ν_{ji} is the stoichiometric coefficient of component i in chemical reaction j and μ_i is its chemical potential. The reaction equilibrium condition for our model reaction, Eq. (3), in CC A (the reaction void) is then

$$\mu_B^A - 2\mu_A^A = 0, \quad (18)$$

where μ_l^A is the chemical potential of component l in CC A. Forward and reverse reaction steps are accepted with probabilities

$$\min \left[1, \frac{\Gamma}{V_A} \frac{N_A^A(N_A^A - 1)}{N_B^A + 1} \exp \left(-\frac{\Delta U_A}{k_B T} \right) \right] \quad (19)$$

and

$$\min \left[1, \frac{V_A}{\Gamma} \frac{N_B^A}{(N_A^A + 1)(N_A^A + 2)} \exp \left(-\frac{\Delta U_A}{k_B T} \right) \right], \quad (20)$$

respectively. In Eqs. (19) and (20), V_A is the volume of CC A, Γ is the ideal-gas quantity defined as

$$\Gamma = \frac{k_B T}{P^0} K, \quad (21)$$

where P^0 is the standard state pressure of 1 bar, K is the equilibrium constant,²⁹ N_l^A is the number of particles of component l in CC A, and ΔU_A is the change in the configurational energy U due to forward and reverse reaction attempts in CC A.

C. Imposed pressure gradient (GCMC)

In order to maintain a flux of particles through the membrane, we impose a pressure gradient across it. The pressure gradient is indirectly controlled by performing GCMC particle insertion and deletion steps in CC B (the transport void) only. According to the GCMC algorithm,¹⁹ the chemical potential of component l in CC B, μ_l^B , is chosen and the creation and destruction of a particle of component l is accepted with probabilities

$$\min \left[1, \frac{V_B q_l(T)}{N_l^B + 1} \exp \left(\frac{\mu_l^B}{k_B T} \right) \exp \left(-\frac{\Delta U_B}{k_B T} \right) \right] \quad (22)$$

and

$$\min \left[1, \frac{N_l^B}{V_B q_l(T)} \exp \left(-\frac{\mu_l^B}{k_B T} \right) \exp \left(-\frac{\Delta U_B}{k_B T} \right) \right], \quad (23)$$

respectively. In Eqs. (22) and (23), V_B is the volume of CC B, $q_l(T)$ is the internal contribution of the partition function for component l , N_l^B is the number of particles of component l in CC B, and ΔU_B is the change in the configurational energy U due to creation and destruction attempts in CC B.

III. ILLUSTRATIVE APPLICATION: A NANOSCALE MEMBRANE REACTOR MODEL

We applied the DCC-RxMD method to simulate a multicomponent system in which both a chemical reaction and physisorption is occurring within a nanoporous solid. We consider the dry reforming of methane reaction which is an important industrial process for producing syngas (H_2/CO) from CH_4 and CO_2 .²⁰ We demonstrate how the reaction conversion is affected by separating out H_2 from the reaction mixture via a semipermeable membrane. Below we provide

details of the reaction species models, membrane models, and further computational information specific to such the DCC-RxMD application.

A. Reaction species potential models

We consider a nanoscale membrane reactor model (described in the preceding section, see also Fig. 1) in which the dry reforming reaction



occurs in the reaction void (CC A) and the membrane is (preferentially) permeable to H_2 . A difference in the H_2 partial pressures between the reaction and transport voids, i.e., between CC A and CC B will result in a H_2 flux through the membrane. REMC forward and reverse reaction steps for the reaction shown in Eq. (24) are accepted with probabilities

$$\min \left[1, V_A^2 \Gamma \frac{N_{CH_4}^A N_{CO_2}^A}{(N_{H_2}^A + 1)(N_{H_2}^A + 2)(N_{CO}^A + 1)(N_{CO}^A + 2)} \times \exp \left(-\frac{\Delta U_A}{k_B T} \right) \right] \quad (25)$$

and

$$\min \left[1, \frac{1}{V_A^2 \Gamma} \frac{(N_{H_2}^A - 1)N_{H_2}^A(N_{CO}^A - 1)N_{CO}^A}{(N_{CH_4}^A + 1)(N_{CO_2}^A + 1)} \exp \left(-\frac{\Delta U_A}{k_B T} \right) \right], \quad (26)$$

respectively, where Γ is defined as

$$\Gamma = \left(\frac{P^0}{k_B T} \right)^2 K \quad (27)$$

and K is evaluated using the JANAF Tables.³⁰

Components of the reaction system CH_4 , CO_2 , H_2 , and CO are modeled as Lennard-Jones (LJ) spheres. The fluid-fluid interactions are approximated with a truncated-and-shifted LJ (TS-LJ) potential

$$u^{\text{TS-LJ}}(r_{ij}) = u^{\text{LJ}}(r_{ij}) - u_c^{\text{LJ}}, \quad r_{ij} \leq r_{c,ab} \quad (28)$$

$$= 0, \quad r_{ij} > r_{c,ab}, \quad (29)$$

where

$$u^{\text{LJ}}(r_{ij}) = 4\epsilon_{ab} \left[\left(\frac{\sigma_{ab}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ab}}{r_{ij}} \right)^6 \right], \quad (30)$$

$$u_c^{\text{LJ}} = 4\epsilon_{ab} \left[\left(\frac{\sigma_{ab}}{r_{c,ab}} \right)^{12} - \left(\frac{\sigma_{ab}}{r_{c,ab}} \right)^6 \right]. \quad (31)$$

Here, r_{ij} is the distance between particle i for component a and particle j for component b , ϵ 's and σ 's are the effective LJ energy and size parameters, respectively, and $r_{c,ab}$ is the spherical cutoff distance assigned to be $r_{c,ab} = 3.5\sigma_{ab}$. The ϵ 's and σ 's for CH_4 , CO_2 , and H_2 were taken from Ref. 31, those for CO were taken from Ref. 32 and are listed in Table I. The cross-term LJ parameters were evaluated using the Lorentz-Berthelot combining rules,¹⁸

TABLE I. Effective LJ energy (ϵ) and size (σ) parameters for CH₄, CO₂, H₂ (Ref. 31) and CO (Ref. 32) fluids, and membrane particles (Ref. 36).

Component	ϵ/k_B (K)	σ (nm)
CH ₄	148.1	0.3810
CO ₂	225.3	0.3794
H ₂	38.0	0.290
CO	123.0	0.3662
Membrane	82.0	0.270

$$\epsilon_{ab} = \sqrt{\epsilon_{aa}\epsilon_{bb}}, \quad (32)$$

$$\sigma_{ab} = \frac{\sigma_{aa} + \sigma_{bb}}{2}. \quad (33)$$

Firouzi *et al.*³³ have confirmed that these LJ models for CH₄, CO₂, H₂, and CO produced a phase diagram and thermodynamic properties which are in quantitative agreement with the experimental data, under both subcritical and supercritical conditions.

Fluid particles of component l interact with the repulsive confining walls w (see Fig. 1) via the TS-LJ potential with ϵ_{lw} , σ_{lw} , and $r_{c,lw} = 2^{1/6}\sigma_{lw}$. For simplicity, we use $\epsilon_{lw} \equiv \epsilon_{ll}$ and $\sigma_{lw} \equiv \sigma_{ll}$ since the confining walls have no direct influence on the transport in the membrane region and have only small effects on fluid properties in the portions of CCs adjacent to the confining walls.

B. Membrane models

In order to increase the reaction conversion in our nanomembrane reactor model by separating out a particular product from the mixture, it is required that the membrane separating the reaction and transport voids be permeable to that particular product only. For the dry reforming of methane reaction considered here, we define our membrane model to be permeable to H₂ only while being impermeable to the remaining reaction species, namely, CH₄, CO₂, and CO. Since the dry reforming reaction is typically carried out at quite high temperatures, in general, the separation of mixture components via a membrane is based primarily on molecular sieving caused by the passage of smaller molecules of the mixture through the pores while the larger molecules are obstructed.³⁴ As evident in Table I, H₂ molecules are smaller than the CH₄, CO₂, and CO molecules. Hence, a characteristic size for the membrane pores should be greater than σ_{H_2} (to allow H₂ to permeate through the membrane) but yet less than or comparable to $\sigma_{CH_4} \approx \sigma_{CO_2} \approx \sigma_{CO}$ (to obstruct CH₄, CO₂, and CO from permeating through the membrane).

We utilized two types of membrane models. The first model, proposed by Powles *et al.*,^{25,35} defines membranes by several layers of LJ particles (characterized by the energy and size parameters ϵ_m and σ_m , respectively) with a distance between layers equal to $2^{1/6}\sigma_m$ (which corresponds to the LJ potential minimum). The particles in each layer are arranged in a face-centered cubic (fcc) structure. The layers are built by replicating a four-particle fcc primitive cell in the y and z directions. A two-dimensional schematic of a layer of particles for this model, termed the Powles' membrane

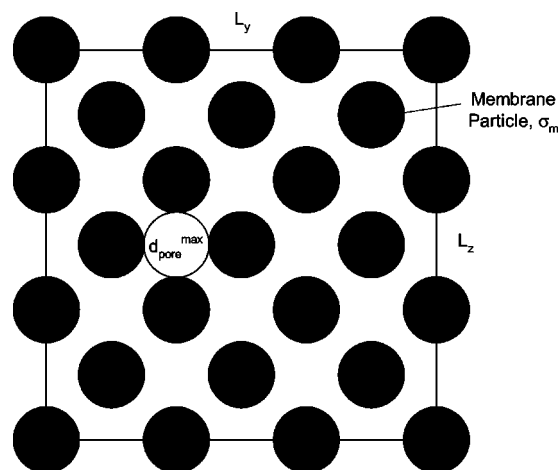


FIG. 2. Schematic of a fcc membrane layer for the Powles' membrane model discussed in text. The size of the particles making up the membrane is characterized by σ_m . An open circle of diameter d_{pore}^{max} indicates the maximum size of a membrane pore.

model (PM), is shown in Fig. 2. Also shown is the maximum allowable size d_{pore}^{max} for a pore in the membrane structure. Chosen values for ϵ_m and σ_m correspond to silicalite molecules³⁶ and are listed in Table I. The membrane particles interact with fluid particles via the TS-LJ potential, Eqs. (28) and (29), and with the cross-term LJ parameters evaluated from the Lorentz-Berthelot combining rules, Eqs. (32) and (33). Powles' model generates membranes with well-defined structures comprising straight channels that are prototypical of zeolitic structures. We built two Powles' membranes and denote them PM1 and PM2. Both models consist of seven fcc layers but differ by their values of d_{pore}^{max} . PM1 has $d_{pore}^{max} = 0.3253$ nm which corresponds to a membrane number density $\rho_m = 21.728$ nm⁻³ while PM2 is characterized by $d_{pore}^{max} = 0.4104$ nm and $\rho_m = 16.635$ nm⁻³. Geometric pore size distributions³⁷ (PSDs) for PM1 and PM2 are displayed in Fig. 3. As expected, Fig. 3 shows PSDs that are quite narrow with maximum peaks corresponding to d_{pore}^{max} .

The second type of membrane model used in this study comprises random configurations of nonoverlapping LJ spheres. The model, termed the random membrane model (RM), is generated from a canonical Monte Carlo simulation of hard spheres with a corresponding diameter of σ_m .³⁸ We built RMs with various PSDs in the volume $2L_{1x} \times L_y \times L_z$ where the same value of L_{1x} as in PM1 and PM2 is used. We then chose one RM whose PSD peak is roughly at the same position as the PSD peak for PM2. The chosen RM has $\rho_m = 15.156$ nm⁻³ and its PSD is displayed in Fig. 3. Figure 3 shows that the PSD for the RM is substantially broader than that of PM2 due to the random arrangement of the membrane particles.

C. Computational details

In addition to the DCC-RxMD simulations, we also carried out DCV-GCMD simulations for pure CH₄, CO₂, H₂, and CO, and an equimolar mixture of CH₄/CO₂/H₂/CO. In the DCV-GCMD simulations both CCs are used to maintain constant chemical potentials for the particular components.

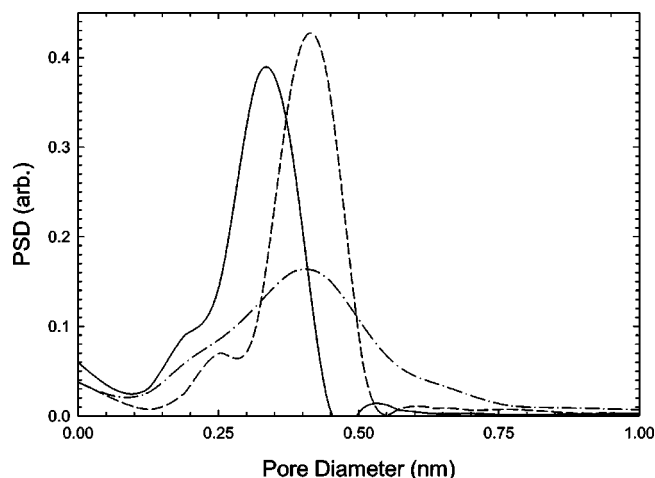


FIG. 3. Computed geometric pore size distributions (PSD) for the three membrane models: PM1 (—), PM2 (---), and RM (-·-·-). Units for the y coordinates are arbitrary.

Setting different values for the chemical potentials in CC A and CC B results in different pressures in these CCs. The imposed pressure gradient across the membrane causes a flux of fluid particles through the membrane. Hence, the DCV-GCMD simulations enable us to investigate properties of the membranes PM1, PM2, and RM independent of chemical reaction behavior. For the DCV-GCMD and DCC-RxMD simulation boxes, we used $L_{1x}=L_{2x}=0.909\,066$ nm ($L_{1x}=0.909\,066$ nm corresponds to seven membrane layers in PM1 and PM2), $L_{3x}=18.288$ nm, $L_{4x}=19.050$ nm, and $L_y=L_z=9.525$ nm. Use of $L_{1x}=L_{2x}$ (see Fig. 1) minimizes possible steric hindrance effects at the entrance of the membrane pores.³⁹

After some preliminary test runs, we found that $n_{MD}=10$, $n_{REMC}=300$, and $n_{GCMC}=300$ are satisfactory values to properly maintain reaction equilibrium in CC A, constant chemical potentials in CC B, and reasonable transport rates at the boundaries between the CCs and the membrane region. Typically, there are 600 fluid particles in CC A and 10–500 fluid particles in CC B. Simulations were started with particles distributed in CC A and CC B only and no particles in the membrane region. We then carried out typically 0.25 ns simulation runs to achieve steady state. Subsequent production runs ranged from 1 ns for pure DCV-GCMD simulations to 2 ns for mixture DCV-GCMD and DCC-RxMD simulations, where $\Delta t=3.438$ fs.

During the simulation we evaluated the excess internal energy u , number density ρ , pressure P , and compositions x_i^A and x_i^B of the mixtures in the CCs. The pressure was computed from the virial theorem.¹⁸ To minimize the influence of the interfaces between the CCs and the membrane region as well as the effects of the confining walls on the adjacent portions of the CCs, fluid properties in the CCs were calculated in a predetermined interior portion of the CCs. More specifically, the fluid property calculations were applied only to molecules in CCs whose x coordinates were at a distance greater than $\max\{r_{c,lw}\}_{l=1}^4$ from the CCs boundaries. We also calculated the molar flux through the membranes for component l , J_l , and the permeability of compo-

nent l , K_l . J_l was determined from the expression

$$J_l = \frac{N_l^{\text{LTR}} - N_l^{\text{RTL}}}{N_A A_{yz} N_{\text{MDsteps}} \Delta t} \quad (34)$$

and K_l was defined as

$$K_l = \frac{J_l^x}{\Delta P_l / \delta}. \quad (35)$$

In Eqs. (34) and (35), N_l^{LTR} and N_l^{RTL} are the net movement of particles for component l through the yz plane at $x=0$ from left-to-right and from right-to-left, respectively, N_A is Avogadro's number, $A_{yz}=L_y L_z$ is the yz area of the simulation box, N_{MDsteps} is the total number of isothermal MD steps, and $\Delta P_l = x_l^A P_A - x_l^B P_B$ is the partial pressure difference for component l .

IV. RESULTS AND DISCUSSIONS

A. DCV-GCMD

Before presenting results for the increase of reaction conversion by separation of the H_2 product from the reaction mixture of $CH_4/CO_2/H_2/CO$ for the dry reforming reaction, we present results from DCV-GCMD simulations for the pure fluids and equimolar mixtures. The intent is to investigate the properties of the membrane models PM1, PM2, and RM independent of chemical reaction behavior. We performed all simulations at a typical temperature for the dry reforming reaction, $T=1100$ K.²⁰

1. Pure fluids

In the DCV-GCMD simulations for pure CH_4 , CO_2 , H_2 , and CO , we set $\mu^A/(RT) = -4.039$ and varied $\mu^B/(RT)$ from -4.308 to -5.520 ; R is the universal gas constant. This results in a pressure difference $\Delta P = P_A - P_B$ ranging from 7 bars to 37 bars, where $P_A \approx 48$ bars. Figure 4 presents J_l as a function of ΔP for all three membrane models. Values of K_l for the membrane models did not show (within statistical uncertainties) dependence on ΔP . Averaged K_l values are listed in Table II. Figure 4 and Table II show that only PM1 is, strictly speaking semipermeable, i.e., permeable to H_2 and completely impermeable to CH_4 , CO_2 , and CO . Both PM2 and RM exhibit very small yet undesirable permeabilities for CH_4 , CO_2 , and CO in addition to substantial permeability for H_2 . However, semipermeable membranes in industrial membrane reactors also exhibit small undesirable permeabilities for nonseparating components. In the cases of PM2 and RM, typical values of the molar fluxes for CH_4 , CO_2 , and CO are one order smaller than the corresponding values of the molar flux for H_2 . Similar behavior is exhibited for component permeabilities. Note that since $\sigma_{CH_4} \approx \sigma_{CO_2} \approx \sigma_{CO}$ and since at $T=1100$ K values of ϵ 's have only a moderate influence on the transport properties, $J_{CH_4} > J_{CO} > J_{CO_2}$ in the case of PM2 is primarily due to $m_{CH_4} < m_{CO} < m_{CO_2}$. In contrast to PM2 the effect of the different masses of the components on J_l is less pronounced for RM. This is due to the ability of the particles to pass more freely through the straight pores of PM2 as opposed to the contour pores of RM. Also note in Fig. 4 that at the same ΔP , values of J_{H_2}

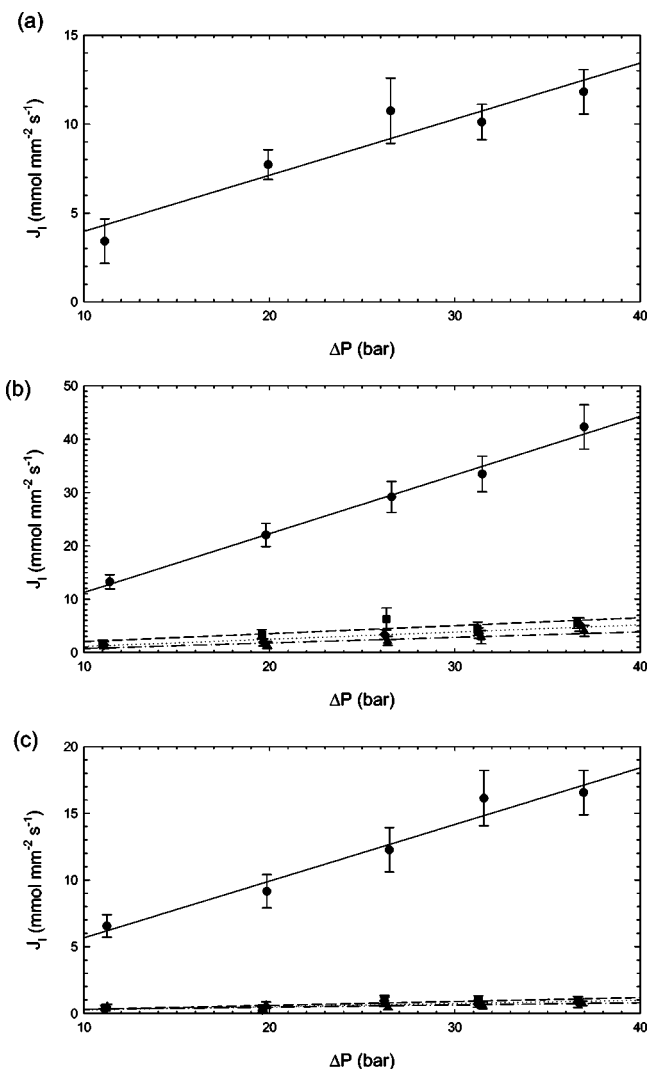


FIG. 4. Molar flux through the membrane models (a) PM1, (b) PM2, and (c) RM for component l , J_l , as a function of the pressure difference ΔP obtained from the DCV-GCMD simulations for pure CH₄ (■), CO₂ (▲), H₂ (●), and CO (◆). Lines serve as a guide to the eye only.

in PM1 are about three times smaller than values of J_{H_2} in PM2. Further, values of J_{H_2} in PM2 are approximately two times larger than those found in RM. This behavior is a consequence of the well defined pore structure of PM2 whose PSD is much narrower compared to the PSD of RM.

Figure 5 shows typical density profiles for H₂ across the membrane models PM1, PM2, and RM at $\Delta P \approx 32$ bars. The high-pressure and low-pressure sides of the membrane correspond to $x \approx -1$ and 1 nm, respectively, implying a flux of H₂ particles from left to right in Fig. 5. The vertical dotted lines denote the membrane model boundaries. The density profiles for PM1 and PM2 exhibit oscillatory character with minimums corresponding to the membrane layers and with maximums at positions between them. The density profile for RM decreases nearly monotonically from the high-pressure to low-pressure membrane sides due to the random configuration of membrane particles in RM. The behavior of the relative permeabilities of H₂ for the different membrane models is reiterated in Fig. 5.

2. Equimolar mixtures

In the DCV-GCMD mixtures simulations, we set $\{\mu_l^A/(RT)\}_{l=1}^4 = \{-5.385, -5.385, -5.385, -5.385\}$ and varied $\{\mu_l^B/(RT)\}_{l=1}^4$ from $\{-5.655, -5.655, -5.655, -5.655\}$ to $\{-6.732, -6.732, -6.732, -6.732\}$ by keeping $\mu_{CH_4}^B = \mu_{CO_2}^B = \mu_{H_2}^B = \mu_{CO}^B$. This results in ΔP ranging from 7 bars to 37 bars, where $P_A \approx 50$ bars. At $T = 1100$ K, mixtures in CC A and CC B are marginally nonideal and hence, the used values of μ_l^A and μ_l^B produce roughly equimolar mixture compositions in both CCs, i.e., $x_l^A \approx x_l^B \approx 0.25$. Plots of J_l as a function of the partial pressure difference ΔP_l for all three membrane models are given in Fig. 6. As in the case of pure fluids, values of K_l did not show (within statistical uncertainties) dependence on ΔP_l (see Table II). From Fig. 6 and Table II we can draw similar conclusions about the dependence of the molar fluxes and permeabilities based on the relative membrane PSDs and structures. The notable difference being that the values of J_l for equimolar mixtures are smaller than corresponding values of J_l for pure fluids since $\Delta P_l \approx 0.25 \Delta P$.

B. DCC-RxMD

At $T = 1100$ K and a bulk volume $V \equiv V_A = (L_{3x} - L_{2x}) \times L_y \times L_z = 1576.71$ nm³, both the REMC and RxMD predict the following bulk equilibrium properties of the reaction mixture CH₄/CO₂/H₂/CO: $u = -0.057_{26}$ kJ mol⁻¹, $P = 50.7_{11}$ bars, $\rho = 0.3291_{184}$ nm⁻³, $x_{CH_4} = 0.222_{10}$, $x_{CO_2} = 0.222_{10}$, $x_{H_2} = 0.278_{10}$, and $x_{CO} = 0.278_{10}$; subscripts in numerical values denote the standard deviations in the last digits. Simulations were initiated with $N_{CH_4}^{ini} = N_{CO_2}^{ini} = N_{H_2}^{ini} = N_{CO}^{ini} = 125$ molecules in the simulation box. At equilibrium, the total number of molecules in the bulk reaction system was $N = \sum_{l=1}^4 N_l = 520_5$.

All DCC-RxMD simulations were started with $N_{CH_4}^{ini} = N_{CO_2}^{ini} = N_{H_2}^{ini} = N_{CO}^{ini} = 125$ in CC A, i.e., with $N_A^{ini} = 500$. Values of μ_l^B were chosen in such a way to obtain virtually pure H₂ in CC B. This was achieved by setting $\mu_{CH_4}^B/(RT) = \mu_{CO_2}^B/(RT) = \mu_{CO}^B/(RT) = -12.117$. Values of $\mu_{H_2}^B/(RT)$ were then varied from -4.712 to -8.078 . This results in $\Delta P > 0$ but $\Delta P_{H_2} < 0$ for $\mu_{H_2}^B/(RT) > -5.25$ and $\Delta P_{H_2} > 0$ otherwise. Note that the pressure in the reaction void decreases with the removal of H₂ since the total number of particles decreases (see Figs. 7–9). For $\Delta P_{H_2} < 0$, H₂ flows from the transport void to the reaction void while for $\Delta P_{H_2} > 0$, there is a H₂ flux from the reaction void to the transport void. Further, $\mu_{H_2}^B/(RT) = -8.078$ produces nearly vacuum conditions in CC B, i.e., the equilibrium number of particles in CC B becomes very small and thus $P_B \rightarrow 0$. Hence, the value of ΔP_{H_2} resulting from $\mu_{H_2}^B/(RT) = -8.078$ corresponds roughly to the maximum achievable ΔP_{H_2} .

Figures 7–9 show J_{H_2} and N_A/N_A^{ini} , and x_l^A as a function of ΔP_{H_2} for all three membrane models. Note that x_l^A at $\Delta P_{H_2} = 0$ corresponds to x_l^A of the bulk reaction system. We see from Figs. 7–9 that the maximal ΔP_{H_2} [corresponding to $\mu_{H_2}^B/(RT) = -8.078$] is directly related to values of

TABLE II. Permeabilities K_l obtained from the DCV-GCMD simulations of pure CH_4 , CO_2 , H_2 , and CO , and an equimolar mixture of $\text{CH}_4/\text{CO}_2/\text{H}_2/\text{CO}$ for all three membranes PM1, PM2, and RM. Subscripts in table values denote the standard deviations in the last digits.

Membrane	Pure fluids			
	$K_{\text{CH}_4} \times 10^6$ (mmol bar ⁻¹ mm ⁻¹ s ⁻¹)	$K_{\text{CO}_2} \times 10^6$ (mmol bar ⁻¹ mm ⁻¹ s ⁻¹)	$K_{\text{H}_2} \times 10^6$ (mmol bar ⁻¹ mm ⁻¹ s ⁻¹)	$K_{\text{CO}} \times 10^6$ (mmol bar ⁻¹ mm ⁻¹ s ⁻¹)
PM1	0 ₉	0 ₉	400 ₅₀	15 ₁₅
PM2	200 ₄₀	77 ₅₅	1270 ₄₀	145 ₉
RM	35 ₉	35 ₂₀	570 ₆₀	35 ₉
Membrane	Equimolar mixture			
	$K_{\text{CH}_4} \times 10^6$ (mmol bar ⁻¹ mm ⁻¹ s ⁻¹)	$K_{\text{CO}_2} \times 10^6$ (mmol bar ⁻¹ mm ⁻¹ s ⁻¹)	$K_{\text{H}_2} \times 10^6$ (mmol bar ⁻¹ mm ⁻¹ s ⁻¹)	$K_{\text{CO}} \times 10^6$ (mmol bar ⁻¹ mm ⁻¹ s ⁻¹)
PM1	9 ₉	0 ₉	450 ₆₀	0 ₉
PM2	180 ₉	95 ₂₅	1270 ₇₀	120 ₄₀
RM	25 ₃₀	20 ₂₀	575 ₁₂₀	35 ₂₅

K_{H_2} : a membrane model with a larger K_{H_2} has a lower ΔP_{H_2} (cf., e.g., the case of PM2 with $K_{\text{H}_2} \approx 1270 \times 10^{-6}$ mmol bar⁻¹ mm⁻¹ s⁻¹ and maximal $\Delta P_{\text{H}_2} \approx 3$ bars with the case of PM1 with $K_{\text{H}_2} \approx 400 \times 10^{-6}$ mmol bar⁻¹ mm⁻¹ s⁻¹ and maximal $\Delta P_{\text{H}_2} \approx 8$ bars). Also note that the upper portions of Figs. 7–9 show that the values of J_{H_2} corresponding to the maximal ΔP_{H_2} are approximately the same. In contrast to these values of J_{H_2} , the values of N_A/N_A^{ini} at the maximal ΔP_{H_2} differ significantly; they are lower for membranes with a higher K_{H_2} . Next note that compositions x_l^A as a function of ΔP_{H_2} in the lower portions of Figs. 7–9 show that the compositions of reactants CH_4 and CO_2 decrease slowly with increasing ΔP_{H_2} (except $x_{\text{CH}_4}^A$ and $x_{\text{CO}_2}^A$ close to the maximal ΔP_{H_2} for PM2). The composition of the product

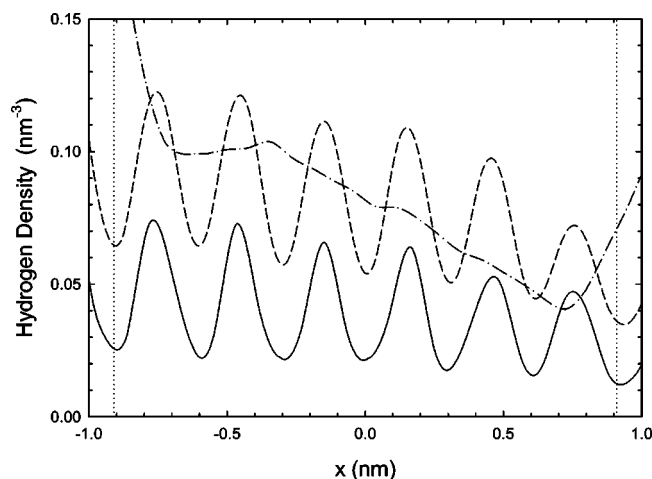


FIG. 5. Density profiles for H_2 across the membrane models PM1 (—), PM2 (---), and RNM (- · - · -) at $\Delta P \approx 32$ bars. The dotted lines denote the membrane boundaries. H_2 molecules are flowing from left-to-right due to the imposed pressure gradient.

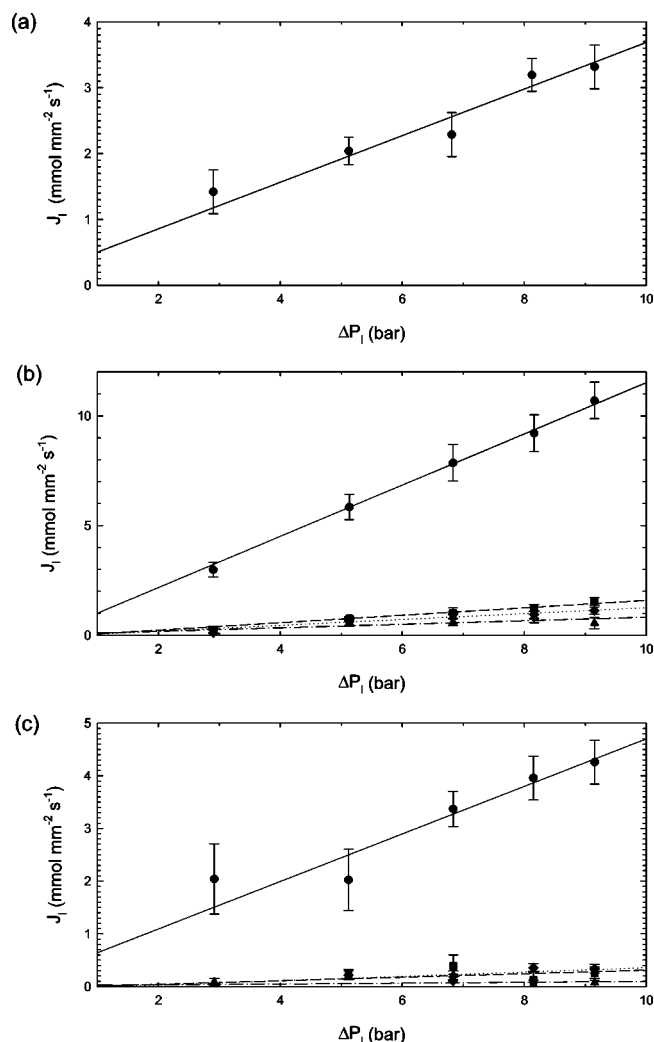


FIG. 6. Molar flux through the membrane models (a) PM1, (b) PM2, and (c) RM for component l , J_l , as a function of the partial pressure difference ΔP_l obtained from the DCV-GCMD simulations for equimolar mixtures of CH_4 (■)/ CO_2 (▲)/ H_2 (●)/ CO (◆). Lines serve as a guide to the eye only.

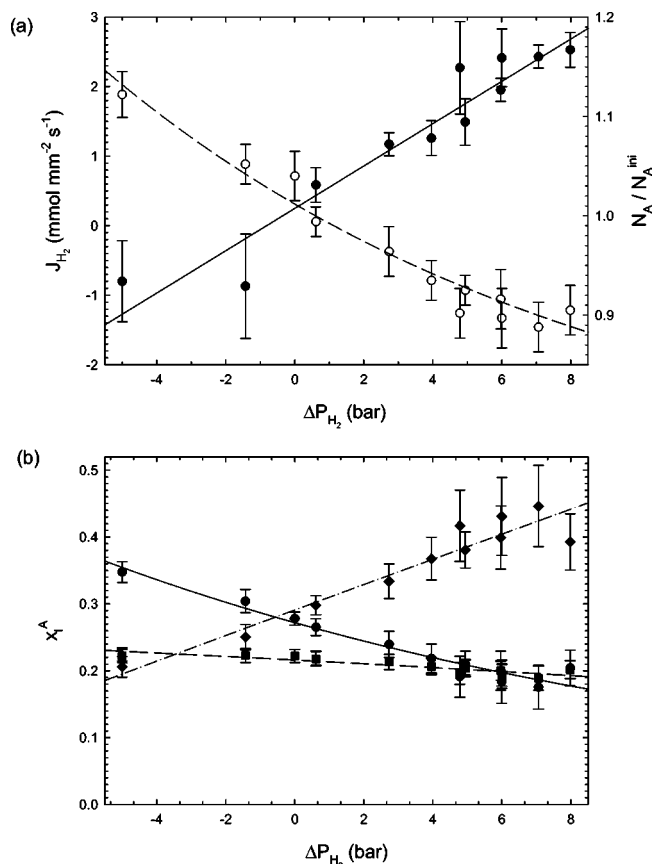


FIG. 7. (a) Hydrogen molar flux J_{H_2} (●) and N_A/N_A^{ini} (○) as a function of the hydrogen partial pressure difference ΔP_{H_2} , and (b) the composition in the reaction void x_i^A (CH₄, ■; H₂, ●; CO, ◆) as a function of ΔP_{H_2} in the case of PM1 obtained from the DCC-RxMD simulations. Due to identical initial compositions of CH₄ and CO₂ $x_{CH_4}^A = x_{CO_2}^A$ within statistical uncertainties, therefore $x_{CO_2}^A$ is not plotted. Lines serve as a guide to the eye only.

CO increases significantly with increasing ΔP_{H_2} . At the maximal ΔP_{H_2} , x_{CO}^A is larger for membranes with a larger K_{H_2} . With respect to x_{CO}^A at $\Delta P_{H_2} = 0$, increases of x_{CO}^A at the maximal ΔP_{H_2} are $\sim 60\%$ for PM1, $\sim 80\%$ for RM, and $\sim 150\%$ for PM2. $x_{H_2}^A$ decreases with increasing ΔP_{H_2} due to hydrogen separation from the reaction void to the transport void. The decrease of $x_{H_2}^A$ is related to K_{H_2} and is larger for membrane models with larger K_{H_2} . The total yield of H₂ is a result of the H₂ amount in both the reaction and transport voids.

V. CONCLUSIONS

We have presented a simulation tool, termed the dual control cell reaction ensemble molecular dynamics (DCC-RxMD) method, to study fluid mixtures that are simultaneously chemically reacting and adsorbing in a porous material. The DCC-RxMD method was developed by coupling a nonequilibrium molecular dynamics method with two Monte Carlo based methods, namely, reaction ensemble Monte Carlo (REMC) and grand canonical Monte Carlo (GCMC). Control cells, which are in direct physical contact with the porous solid, are used to maintain the desired reac-

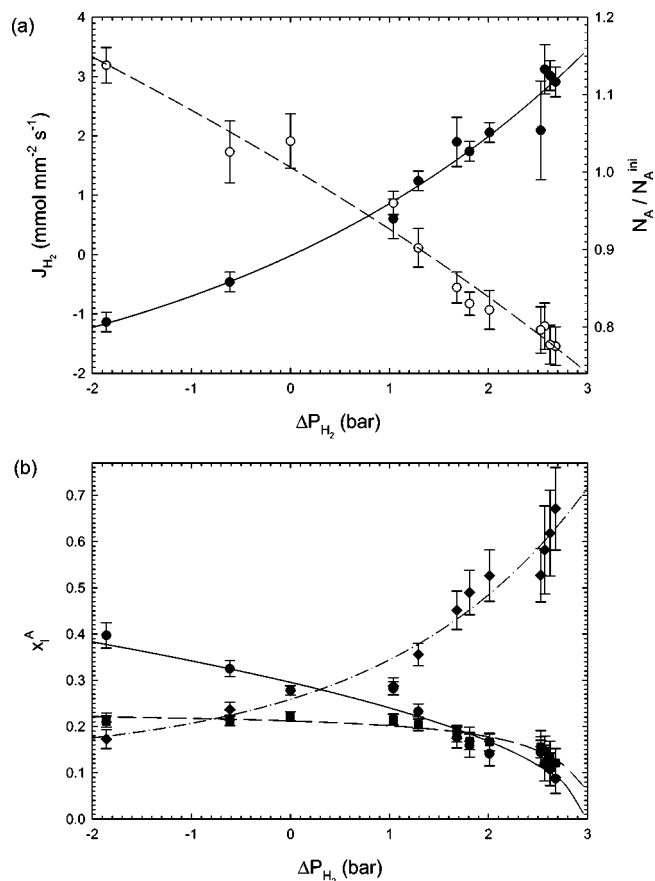


FIG. 8. (a) Hydrogen molar flux J_{H_2} (●) and N_A/N_A^{ini} (○) as a function of the hydrogen partial pressure difference ΔP_{H_2} , and (b) the composition in the reaction void x_i^A (CH₄, ■; H₂, ●; CO, ◆) as a function of ΔP_{H_2} in the case of PM2 obtained from the DCC-RxMD simulations. Due to identical initial compositions of CH₄ and CO₂ $x_{CH_4}^A = x_{CO_2}^A$ within statistical uncertainties, therefore $x_{CO_2}^A$ is not plotted. Lines serve as a guide to the eye only.

tion and flow conditions. The simulation setup closely mimics an actual experimental system in which the thermodynamic and flow parameters are precisely controlled. The method is akin to the dual control volume grand canonical molecular dynamics method that was developed to study the transport properties of fluid mixtures primarily in confined systems. The added feature of the DCC-RxMD method is the inclusion of chemical reactions, thus its applicability is to a wider range of processes beyond solely adsorption phenomena. The method presented here allows for the calculation of both equilibrium and nonequilibrium transport properties in porous materials such as diffusion coefficients, permeability, and mass flux. Effects on these properties due to the characteristics of the porous material can be predicted; characteristics such as the pore size distribution, connectivity, porosity, and surface area. Note that the DCC-RxMD method reduces to the RxMD method¹¹ if the REMC steps are performed in both control cells. Also note that in general, neither the DCC-RxMD nor the RxMD methods can provide reaction rate information but in turn, neither method is limited by reaction rates or activation energy barriers.

As an illustration of the method, we simulated the dry reforming of methane reaction within a nanoscale reactor model in the presence of a semipermeable membrane that

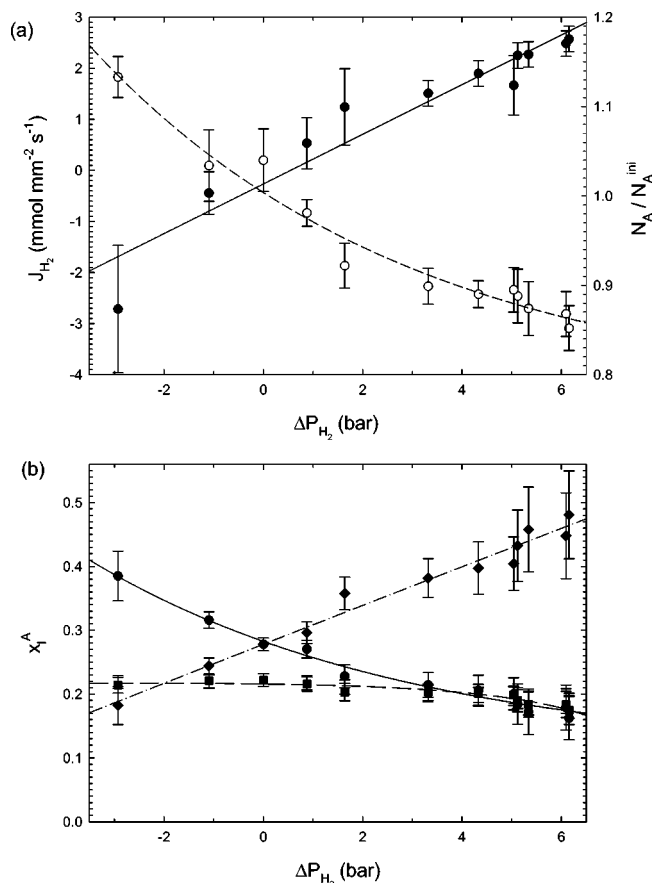


FIG. 9. (a) Hydrogen molar flux J_{H_2} (●) and N_A/N_A^{ini} (○) as a function of the hydrogen partial pressure difference ΔP_{H_2} , and (b) the composition in the reaction void x_i^A (CH_4 , ■; H_2 , ●; CO , ◆) as a function of ΔP_{H_2} in the case of RM obtained from the DCC-RxMD simulations. Due to identical initial compositions of CH_4 and CO_2 $x_{\text{CH}_4}^A = x_{\text{CO}_2}^A$ within statistical uncertainties, therefore $x_{\text{CO}_2}^A$ is not plotted. Lines serve as a guide to the eye only.

was modeled as silicalite. We studied the effects of the membrane structure and porosity on the reaction species permeability by considering three different membrane models. We also studied the effects of an imposed pressure gradient across the membrane on the mass flux of the reaction species. The conversion of syngas (H_2/CO) increased significantly in all the nanomembrane reactor models considered. An increase of 60% at the maximal imposed pressure occurred in the nanomembrane reactor model with a membrane that was exclusively permeable to H_2 . The larger increase (80% and 150% at the maximal imposed pressures) occurred in the nanomembrane reactor models with membranes that exhibited larger values of H_2 permeability but at the same time possessed very small yet undesirable permeabilities for the nonseparating components CH_4 , CO_2 , and CO .

In the application of the DCC-RxMD method presented here, we considered membrane models that did not exhibit attractive character towards the reaction species. Further simulations that include effects of the relative adsorption behavior of the reaction species would be worthwhile. Here again such simulations could provide insight into the membrane characteristics that would most influence the conversion of reactants to products. Further, we note that analogous to the REMC method, multiple reactions can be simulated

simultaneously in the DCC-RxMD method; providing a means of studying systems in which competing reactions play a crucial role. Finally, we should note that in this study, the DCC-RxMD method was applied to a system where a semipermeable membrane exists between the reaction and transport voids. However, this could be any type of porous solid model, be it a simpler slitpore model²¹ or a more realistic model such as an activated carbon.⁴⁰ Within the limit of the available computational resources, DCC-RxMD simulations could also include porous solids on a longer length scale such as microporous solids.

ACKNOWLEDGMENTS

This research was supported by the Grant Agency of the Czech Republic (Grant No. 203/02/0805), by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. IAA4072102), and by the National Research Council of Canada (Grant No. OGP 1041). J.K.B. gratefully acknowledges support from the National Research Council through the U.S. Army Research Laboratory. F.R.S. gratefully acknowledges the support from the MCyT in the program Ramón y Cajal.

¹*Beyond the Molecular Frontier. Challenges for Chemistry and Chemical Engineering*, edited by R. Breslow and M. V. Tirrell (National Academic, Washington, DC, 2003).

²L. D. Gelb, K. E. Gubbins, R. Radhakrishnan, and M. Sliwinski-Bartkowiak, Rep. Prog. Phys. **62**, 1573 (1999).

³C. H. Turner, J. K. Johnson, and K. E. Gubbins, J. Chem. Phys. **114**, 1851 (2001).

⁴C. H. Turner, J. Pikunic, and K. E. Gubbins, Mol. Phys. **99**, 1991 (2001).

⁵C. H. Turner, J. K. Brennan, J. K. Johnson, and K. E. Gubbins, J. Chem. Phys. **116**, 2138 (2002).

⁶M. Borówko, A. Patrykiewicz, S. Sokołowski, R. Zagórski, and O. Pizio, Czech. J. Phys. **48**, 371 (1998).

⁷M. Borówko and R. Zagórski, J. Chem. Phys. **114**, 5397 (2001).

⁸W. R. Smith and B. Třiska, J. Chem. Phys. **100**, 3019 (1994).

⁹J. K. Johnson, A. Z. Panagiotopoulos, and K. E. Gubbins, Mol. Phys. **81**, 717 (1994).

¹⁰M. Lísál, I. Nezbeda, and W. R. Smith, J. Chem. Phys. **110**, 8597 (1999).

¹¹J. K. Brennan, M. Lísál, K. E. Gubbins, and B. M. Rice, Phys. Rev. E (in press).

¹²A. Papadopoulos, E. D. Becker, M. Lupkowski, and F. van Swol, J. Chem. Phys. **98**, 4897 (1993).

¹³K. K. Sirkar, P. V. Schanbhag, and A. S. Kovvali, Ind. Eng. Chem. Res. **38**, 3715 (1999).

¹⁴G. S. Heffelfinger and F. van Swol, J. Chem. Phys. **100**, 7548 (1994).

¹⁵J. M. D. MacElroy, J. Chem. Phys. **101**, 5274 (1994).

¹⁶M. G. Martin, A. P. Thompson, and T. N. Nenoff, J. Chem. Phys. **114**, 7174 (2001).

¹⁷G. Arya, H.-C. Chang, and E. J. Maginn, J. Chem. Phys. **115**, 8112 (2001).

¹⁸M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).

¹⁹D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Academic, London, 2002).

²⁰A. Basile and L. Paturzo, Catal. Today **67**, 55 (2001).

²¹D. Nicholson and N. G. Parsonage, *Computer Simulation and the Statistical Mechanics of Adsorption* (Academic, New York, 1982).

²²R. F. Cracknell, D. Nicholson, and N. Quirke, Phys. Rev. Lett. **74**, 2463 (1995).

²³D. J. Evans and G. P. Morris, *Statistical Mechanics of Nonequilibrium Liquids* (Academic, London, 1990).

²⁴D. J. Evans, W. G. Hoover, B. H. Failor, B. Moran, and A. J. C. Ladd, Phys. Rev. A **28**, 1016 (1983).

²⁵E. Enciso, N. G. Almarza, S. Murad, and M. A. Gonzalez, Mol. Phys. **100**, 2337 (2002).

²⁶D. Brown and J. H. R. Clarke, Mol. Phys. **51**, 1243 (1984).

- ²⁷B. M. Rice, W. Mattson, J. Grosh, and S. F. Trevino, *Phys. Rev. E* **53**, 623 (1996).
- ²⁸S. J. Stuart, A. B. Tutein, and J. A. Harrison, *J. Chem. Phys.* **112**, 6472 (2000).
- ²⁹W. R. Smith and R. W. Missen, *Chemical Reaction Equilibrium Analysis: Theory and Algorithms* (Wiley-Interscience, New York, 1982), reprinted with corrections (Krieger, Malabar, FLA, 1991).
- ³⁰M. W. Chase, Jr., NIST-JANAF Thermochemical Tables, 4th ed., *J. Phys. Chem. Ref. Data Monogr.* **9** (1985).
- ³¹L. Xu, M. G. Sedigh, T. T. Tsotsis, and M. Sahimi, *J. Chem. Phys.* **112**, 910 (2000).
- ³²M. G. Sedigh, W. J. Onstot, L. Xu, W. L. Peng, T. T. Tsotsis, and M. Sahimi, *J. Phys. Chem. A* **102**, 8580 (1998).
- ³³M. Firouzi, T. T. Tsotsis, and M. Sahimi, *J. Chem. Phys.* **119**, 6810 (2003).
- ³⁴W. A. Steele, *The Interaction of Gases with Solid Surfaces* (Pergamon, Oxford, 1974).
- ³⁵J. G. Powles, S. Murad, and P. V. Ravi, *Chem. Phys. Lett.* **188**, 21 (1992).
- ³⁶M. G. Martin, A. P. Thompson, and T. M. Nenoff, *J. Chem. Phys.* **114**, 7174 (2001).
- ³⁷L. D. Gelb and K. E. Gubbins, *Langmuir* **15**, 305 (1999).
- ³⁸I. A. Park and J. M. D. MacElroy, *Mol. Simul.* **2**, 105 (1989).
- ³⁹D. M. Ford and E. D. Glandt, *J. Membr. Sci.* **107**, 47 (1995).
- ⁴⁰J. Pikunic, C. Clinard, N. Cohaut, K. E. Gubbins, J.-M. Guet, R. J.-M. Pellenq, I. Rannou, and J.-N. Rouzaud, *Proceedings of the Sixth International Symposium on the Characterization of Porous Solids*, edited by F. Rodriguez-Reinoso, B. McEnaney, J. Rouquerol, and K. K. Unger (Elsevier, Amsterdam, 2002), pp. 16–26.

NO. OF
COPIES ORGANIZATION

1 DEFENSE TECHNICAL
(PDF INFORMATION CTR
ONLY) DTIC OCA
8725 JOHN J KINGMAN RD
STE 0944
FORT BELVOIR VA 22060-6218

1 US ARMY RSRCH DEV &
ENGRG CMD
SYSTEMS OF SYSTEMS
INTEGRATION
AMSRD SS T
6000 6TH ST STE 100
FORT BELVOIR VA 22060-5608

1 DIRECTOR
US ARMY RESEARCH LAB
IMNE ALC IMS
2800 POWDER MILL RD
ADELPHI MD 20783-1197

3 DIRECTOR
US ARMY RESEARCH LAB
AMSRD ARL CI OK TL
2800 POWDER MILL RD
ADELPHI MD 20783-1197

ABERDEEN PROVING GROUND

1 DIR USARL
AMSRD ARL CI OK TP (BLDG 4600)

NO. OF
COPIES ORGANIZATION

ABERDEEN PROVING GROUND

5 DIR USARL
 AMSRD ARL WM BD
 J BRENNAN