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Citation: *J. Chem. Phys.* **138**, 124109 (2013); doi: 10.1063/1.4796387

View online: <http://dx.doi.org/10.1063/1.4796387>

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A combined quasi-continuum/Langevin equation approach to study the self-diffusion dynamics of confined fluids

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(Received 20 November 2012; accepted 8 March 2013; published online 28 March 2013)

In this work, we combine our earlier proposed empirical potential based quasi-continuum theory, (EQT) [A. V. Raghunathan, J. H. Park, and N. R. Aluru, *J. Chem. Phys.* **127**, 174701 (2007)], which is a coarse-grained multiscale framework to predict the static structure of confined fluids, with a phenomenological Langevin equation to simulate the dynamics of confined fluids in thermal equilibrium. An attractive feature of this approach is that all the input parameters to the Langevin equation (mean force profile of the confined fluid and the static friction coefficient) can be determined using the outputs of the EQT and the self-diffusivity data of the corresponding bulk fluid. The potential of mean force profile, which is a direct output from EQT is used to compute the mean force profile of the confined fluid. The density profile, which is also a direct output from EQT, along with the self-diffusivity data of the bulk fluid is used to determine the static friction coefficient of the confined fluid. We use this approach to compute the mean square displacement and survival probabilities of some important fluids such as carbon-dioxide, water, and Lennard-Jones argon confined inside slit pores. The predictions from the model are compared with those obtained using molecular dynamics simulations. This approach of combining EQT with a phenomenological Langevin equation provides a mathematically simple and computationally efficient means to study the impact of structural inhomogeneity on the self-diffusion dynamics of confined fluids. © 2013 American Institute of Physics.
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I. INTRODUCTION

With the advent of nanotechnology, molecular diffusion in restricted volume has become an attractive subject of both fundamental investigations and applied research. An understanding of the molecular diffusion process in confined geometries is expected to play an important role in designing novel nanoscale applications such as faster transport, separation, and filtration. In recent decades, molecular simulation methods are extensively used to study the diffusion of fluids confined in slit and cylindrical pores.^{1–3} In a slit pore, diffusion is different in the direction parallel (the *x*- and *y*-directions) and normal (*z*-direction) to the pore wall. This is because, unlike the diffusion parallel to the pore wall, the diffusion in the normal direction is inherently transient; i.e., the mean square displacement (MSD) is bounded by the size of the confined region and at long times approaches a constant value. Therefore, the slope of the MSD for the motion perpendicular to the pore wall changes with time. Though molecular simulation methods have helped tremendously to improve our understanding of the anisotropic diffusion mechanism in nanostructures, there has always been an emphasis on the development of empirical models or theories and novel coarse-grained simulation approaches that can be used to study the dynamical and transport properties of inhomogeneous fluids.

Several approaches have been proposed to study the self-diffusivity of inhomogeneous fluids. Some popular

ones such as local average density model (LADM)^{1–3} and Enskog-like theories^{1,2} have been successfully used for hard-sphere (HS) and simple Lennard-Jones (LJ) fluids to predict the effect of structural inhomogeneity on the average pore diffusivity and the self-diffusivity in the direction parallel to the pore wall. Recently, Goel *et al.*⁴ demonstrated that using classical density functional theory (cDFT) together with bulk structure-property relations, it is possible to make semi-quantitative predictions about the average pore diffusivity of the confined HS fluids. It is now a well understood fact that for simple HS and LJ type fluids, under confinement, the self-diffusivity in the direction parallel to the pore wall is relatively insensitive to the degree of structural inhomogeneity and is primarily determined by the average density of the pore.^{1–3} However, the effect of structural inhomogeneity and geometrical constraint on the self-diffusivity in the direction normal to the pore wall is still not clear. Recently, Liu, Harder, and Berne⁵ proposed a virtual-layer sampling based dual molecular dynamics (MD)-Langevin simulation strategy to predict the position dependent self-diffusivity. In dual MD-Langevin simulation dynamics, the dynamical properties calculated from the MD simulations are matched with those determined from Langevin type dynamics to predict the self-diffusivity of the confined fluid. Also, Mittal *et al.*⁶ have proposed a self-consistent propagator-based formalism to estimate the position-dependent diffusion coefficients from the MD simulation trajectory data. In this work, we combine the empirical potential based quasi-continuum theory (EQT)⁷ with a phenomenological Langevin equation to study the

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impact of structural inhomogeneity on the self-diffusivity of the molecules in the direction normal to the pore wall. The model is used to compute the MSD and survival probability of some important fluids confined in slit pores.

The remainder of the paper is organized as follows: In Sec. II, we discuss the model. Simulation details are provided in Sec. III. In Sec. IV, we use the model to predict the position dependent MSD and survival probability of carbon-dioxide, water, and LJ argon confined inside different size graphite slit pores. The predictions from the model are compared with those obtained from MD simulations. Finally, conclusions are presented in Sec. V.

II. PHENOMENOLOGICAL LANGEVIN EQUATION FOR CONFINED FLUIDS

The Langevin equation for the motion of a particle along the confinement direction (referred to as z -direction) can be written as

$$m \frac{dv_z}{dt} = -\frac{dW(z)}{dz} - \gamma mv_z + R(t), \quad (1a)$$

$$v_z = \frac{dz}{dt}, \quad (1b)$$

where m is the mass of the particle, z and v_z are, respectively, the position and the velocity of the particle, $W(z)$ is the potential of mean force (PMF) profile that gives rise to the structural inhomogeneity ($-\frac{dW}{dz}$ is the mean or average force that a fluid molecule experiences at position z due to its interaction with the wall and surrounding fluid), γ is the static (time (t)-independent) friction coefficient that characterizes the dissipation, and $R(t)$ is an “additive” (z and v_z independent) random force that models the thermal noise of the confined fluid. This model is similar in spirit to the one-dimensional (1D) stochastically damped harmonic oscillator (SDHO) model⁸ that describes the dynamical motion of a particle interacting with a harmonic bath, which is in thermodynamic equilibrium at temperature T , except that the interaction potential here is the PMF profile, which ensures that the structural inhomogeneity (or the solvent structure) due to the confinement is properly included. Thus, the inputs required to simulate the equilibrium dynamics of a particle using the above equations are: (a) the mean force profile, $-\frac{dW}{dz}$, and (b) a random force model $R(t)$ that mimics the thermal noise and the static friction coefficient, γ , of the confined fluid. We now discuss the methods/strategies to determine these inputs.

A. Mean force profile ($-\frac{dW}{dz}$)

The mean force profile of the confined fluid is determined using the empirical potential based quasi-continuum theory, EQT.⁷ EQT is a multiscale theory that seamlessly integrates interatomic potentials describing various atomic interactions into the classical continuum theory to predict the equilibrium structure of confined fluids. In EQT, 1D steady-state Nernst-Planck (NP) equation

$$\frac{d}{dz} \left(\frac{d\rho}{dz} + \frac{\rho}{RT} \frac{dW}{dz} \right) = 0 \quad (2)$$

with boundary conditions

$$\rho(z = 0) = 0, \quad (3a)$$

$$\rho(z = H) = 0, \quad (3b)$$

$$\frac{1}{H} \int_0^H \rho(z) dz = \rho_{avg} \quad (3c)$$

is solved to obtain self-consistent potential and concentration profiles of the confined fluid. In Eqs. (2) and (3), ρ is the fluid concentration, R is the gas constant, T is the temperature, and W is the PMF profile of the confined fluid. H is the dimension of the confining geometry and ρ_{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 of the confined fluid. The development of quasi-continuum potentials for spherical, non-polar LJ fluids (methane, argon, etc.), carbon-dioxide, and water in confined environments is discussed in Refs. 9–12. It should be noted that in quasi-continuum potentials, the molecules are represented by their local density, due to which the molecular information related to the shape of the fluid molecule and the interface topology is lost in EQT. Once the quasi-continuum potentials are developed, they can be used in Eq. (2) to obtain self-consistent density and potential profiles of the confined fluid. A self-consistent numerical implementation of EQT is discussed in Ref. 7. Figures 1(a) and 1(b) show the comparison of the center-of-mass (COM) density and PMF profiles obtained from EQT (solid line) for carbon dioxide and water confined inside a graphite slit with those obtained from MD simulations (open circle). It can be observed that the density and the PMF profiles obtained from EQT are in good agreement with those obtained from MD simulations. The PMF profile, which is a direct output from EQT is used to compute $-\frac{dW}{dz}$ in Eq. (1a).

B. Random force model $R(t)$ and friction coefficient γ

The random force $R(t)$ in Eq. (1a) is usually modeled as a Gaussian random variable. Besides assigning a Gaussian character, the following supplementary hypotheses about the random force are made; since the fluid is in thermodynamic equilibrium, no instant plays a preferential role, and the fluctuation force can be modeled as a stationary random process. As a result, its mean does not depend on time and its autocorrelation does not change when shifted in time. Also, it is reasonable to assume that the average value of the random force vanishes, as it ensures that the average velocity of the particle vanishes at equilibrium. Further, we assume that the thermal force is uncorrelated between two time instances and is independent of the position z and velocity v_z across the confinement. Thus, the thermal noise, $R(t)$, is modeled as a stationary, additive Gaussian variable, with properties

$$\langle R(t) \rangle = 0, \quad (4a)$$

$$\langle R(t)R(t + \tau) \rangle = 2Bm^2\delta(\tau), \quad (4b)$$

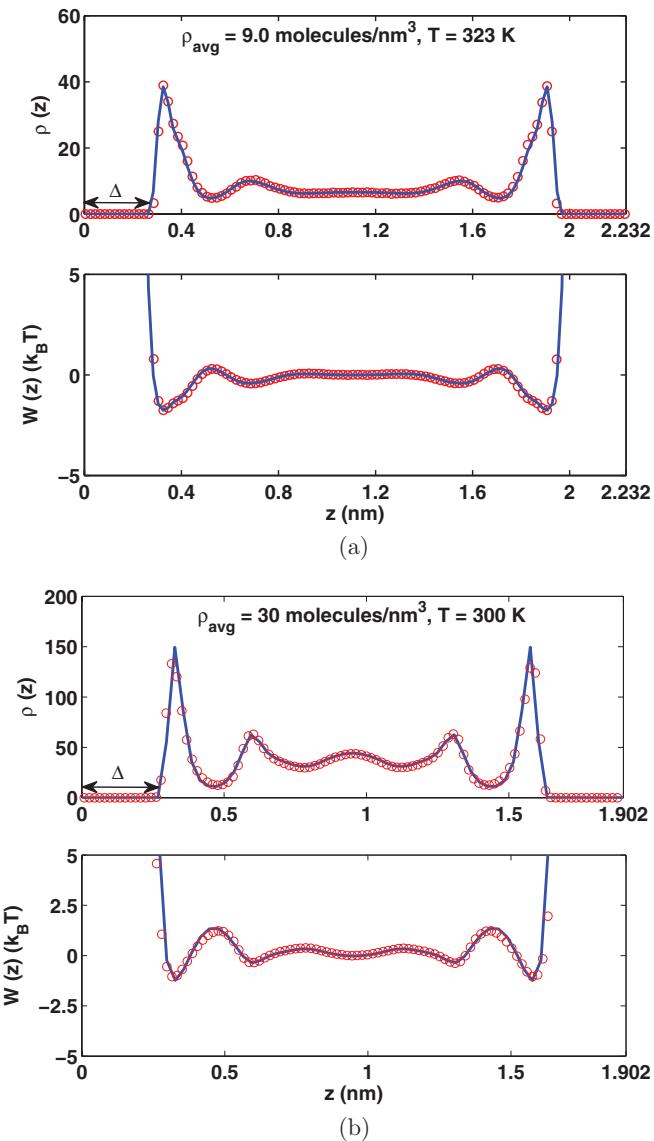


FIG. 1. COM density and PMF profiles of (a) carbon-dioxide, (b) water, confined inside a graphite slit. Δ is the empty region next to the pore wall. Solid line represents the results from EQT and open circle is MD result. The MD simulations details and the computation of the density and PMF profiles from the simulation trajectories are discussed in Refs. 10 and 11.

where $2Bm^2$ (factor $2m^2$ is traditionally taken to simplify the analytical calculation) is the strength of the thermal noise, δ is the Dirac delta function, and angular brackets denote an ensemble average. The thermal noise and the friction coefficient γ are related through fluctuation-dissipation (FD) relations.¹³ Before we derive the FD relations, we investigate using MD simulations, the spatial variation of the thermal noise ($R[t, z]$) in confined fluids. MD simulations are performed in NVE ensemble,¹⁴ where N denotes the number of particles, V the volume, E the total energy, and p the total momentum of the system. The magnitude of thermal force in confinement is computed as

$$R[t, z] = f(t, z) - \langle f(z) \rangle, \quad (5)$$

where, $f(t, z)$ is the total instantaneous force experienced by the particle at position z and time t and $\langle f(z) \rangle$ is the mean de-

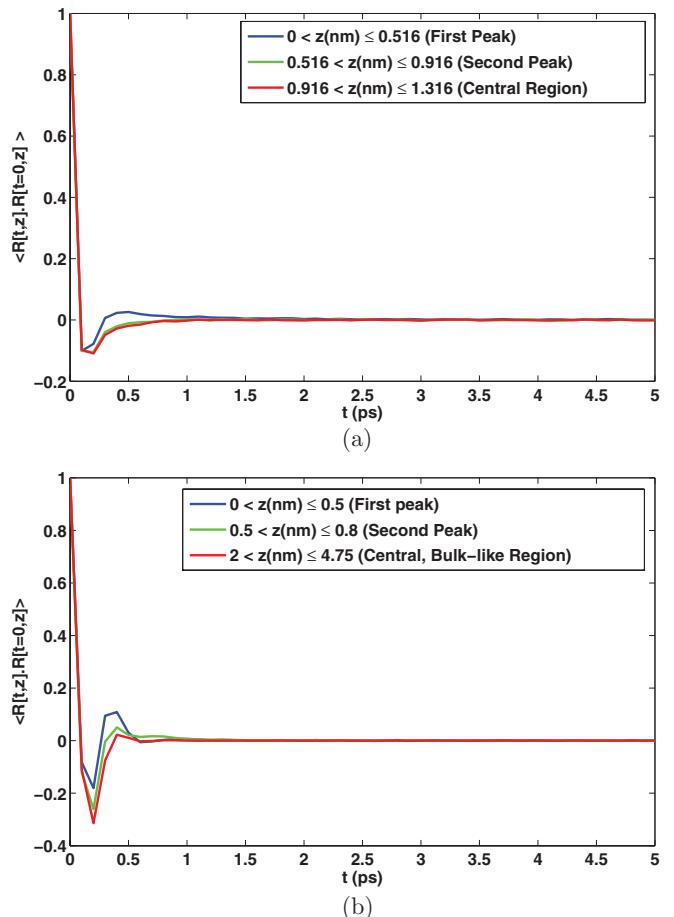


FIG. 2. Spatial variation of thermal noise for (a) carbon-dioxide, (b) LJ argon, confined inside a graphite slit. Thermal-ACFs are normalized by their initial values.

terministic force ($-\frac{dW}{dz}$) experienced by the particle at that position. Figures 2(a) and 2(b) show the autocorrelation function (ACF) of the thermal force computed at different z positions for carbon-dioxide and LJ argon confined inside a graphite slit, respectively. It can be observed that for both fluids, the overall decay behavior of thermal-ACF in different regions is not significantly different from each other. From these observations, it can be inferred that the nature of the thermal force does not change significantly due to the density inhomogeneity at the interface, and as a first approximation it is reasonable to treat thermal noise as spatially invariant (or additive) for confined fluids in thermal equilibrium.

Now we derive the FD relations. Equation (1a) can be solved for the velocity $v_z(t)$ as

$$v_z(t) = v_z(0)e^{-\gamma t} + \frac{1}{m} \int_0^t \left[R(t') - \frac{dW(z(t'))}{dz} \right] \times e^{-\gamma(t-t')} dt', \quad t > 0, \quad (6)$$

where $v_z(0)$ is the initial velocity of the particle. Using the properties of the thermal noise model defined by Eqs. (4a) and (4b), and approximating the value of the mean force $-\frac{dW}{dz}$ at $z(t)$ with its value at the mean position $\langle z(t) \rangle$, the mean and the

TABLE I. Computation of the friction coefficient γ for confined systems.

Confined system	H (nm)	ρ_{avg} (molecules/nm ³)	T (K)	Δ (nm)	ρ_{eff} (molecules/nm ³)	$D(\rho_{eff}, T)$ ($\times 10^{-3}$ nm ² /ps)	γ^a (ps ⁻¹)
CO ₂	2.232	9.0	323	0.27	11.9	16.5	3.69
CO ₂	1.860	8.7	348	0.27	12.3	14.5	4.53
CO ₂	1.488	10.0	323	0.27	15.6	7.0	8.71
SPC/E water	1.902	30	300	0.26	41	1.9	72.8
LJ argon	1.690	18.5	300	0.26	26	3.85	14.7

^aComputed using Eq. (12).

variance of the velocity can be computed as

$$\langle v_z(t) \rangle = v_z(0)e^{-\gamma t} - (1 - e^{-\gamma t}) \frac{dW/dz}{\gamma m} \Big|_{z(t)=\langle z(t) \rangle}, \quad (7)$$

$$\langle [v_z(t) - \langle v_z(t) \rangle]^2 \rangle = \frac{B}{\gamma} (1 - e^{-2\gamma t}), \quad (8)$$

where $-\frac{dW/dz}{\gamma m}$ is the drift velocity imparted to the particle by the potential $W(z)$ at position z . If the potential $W(z)$ is symmetric about z , as is the case for confined fluids in thermal equilibrium (see Fig. 1), then in the long time limit ($t \rightarrow \infty$), the mean position $\langle z(t) \rangle$ will correspond to the minimum energy positions ($\frac{dW}{dz} = 0$), and the mean velocity will be zero. Now, using the equipartition theorem, in the long time limit, the variance of the velocity can be related to the temperature T as

$$\langle [v_z(t) - \langle v_z(t) \rangle]^2 \rangle_{t \rightarrow \infty} = \frac{k_B T}{m}, \quad (9)$$

where k_B is the Boltzmann constant. Comparing Eqs. (8) and (9), we get the first FD relation as

$$\frac{B}{\gamma} = \frac{k_B T}{m} \quad (10)$$

that relates the noise strength to the friction coefficient. This relation ensures that the fluid particle and the thermal bath are in equilibrium with each other at temperature T . Using this relation (Eq. (10)) in Eq. (4b), we get another relation as

$$\gamma = \frac{1}{2mk_B T} \int_{-\infty}^{\infty} \langle R(t)R(t + \tau) \rangle d\tau \quad (11)$$

that relates the ACF of the thermal noise with the friction coefficient γ . This relation is referred to as the second FD relation and is typically used to determine the friction coefficient. The application of this relation to compute the friction coefficient of bulk LJ fluids is discussed in Ref. 14. Also, there is a second approach, generally used for bulk fluids, in which the self-diffusion coefficient, D , can be directly related to the friction coefficient γ through Einstein relation^{13,14} as

$$\gamma = \frac{k_B T}{Dm}. \quad (12)$$

Now, to use these approaches to determine the friction coefficient for confined fluids, we take motivation from the work of Goel *et al.*,⁴ where they identify some static parameters defined by a generalized measure of available or accessible volume that correlate with the single-particle dynamics of confined HS fluids. Here, we define a restricted pore average

density, ρ_{eff} , as

$$\rho_{eff} = \frac{1}{H - 2\Delta} \int_0^H \rho(z) dz = \left(\frac{H}{H - 2\Delta} \right) \rho_{avg}. \quad (13)$$

where H is the width of the slit pore, $\rho(z)$ is the local density of the fluid molecules at position z , Δ is the length of the empty region near the pore wall ($\rho(z) \sim 0$, see Fig. 1), and ρ_{avg} is the average density of the confined fluid. Such accessible volume based definitions of density have been used in Enskog-like theories¹ to explain the oscillatory nature of the solvation force in confined fluids. The local density profile $\rho(z)$ is directly obtained from EQT. Δ is also computed from the density profile $\rho(z)$ and we take it to be the distance until which the density value is less than 0.1 molecules/nm³. Now, for a confined fluid with restricted pore average density ρ_{eff} and temperature T , we assume that its friction coefficient is the same as that of the corresponding bulk fluid at density ρ_{eff} and temperature T . Thus, the determination of the friction coefficient γ of the confined fluid requires computing the restricted pore average density ρ_{eff} (using Eq. (13)) and then performing a quick bulk MD calculation using either of the two approaches (Eqs. (11) and (12)) discussed above. If the self-diffusivity D of the bulk fluid at density ρ_{eff} and temperature T is known *a priori*, then Eq. (12) can be used directly to estimate γ . The computation of the friction coefficient γ for the confined systems considered in this work is discussed in Sec. IV and reported in Table I. For bulk carbon-dioxide, the self-diffusivity data in the temperature range of 243–374 K can be found in Ref. 15. Once the friction coefficient is determined, the strength of the noise can be computed using the first FD relation (Eq. (10)) and the Langevin model (Eqs. (1a) and (1b)) can be solved numerically (see Sec. III) to simulate the equilibrium dynamics of confined fluids.

III. SIMULATION DETAILS

The Langevin equations (Eqs. (1a) and (1b)) are solved numerically using the stochastic version of the Verlet algorithm as¹⁶

$$z^{(1)} = z_t + \frac{1}{2} v_t \Delta t, \quad (14a)$$

$$v_{t+\Delta t} = \frac{\left(1 - \frac{\gamma \Delta t}{2}\right) v_t + m^{-1} F^{(1)} \Delta t + \sqrt{2\gamma k_B T \Delta t / m} \times \eta}{\left(1 + \frac{\gamma \Delta t}{2}\right)}, \quad (14b)$$

$$z_{t+\Delta t} = z^{(1)} + \frac{1}{2} v_{t+\Delta t} \Delta t, \quad (14c)$$

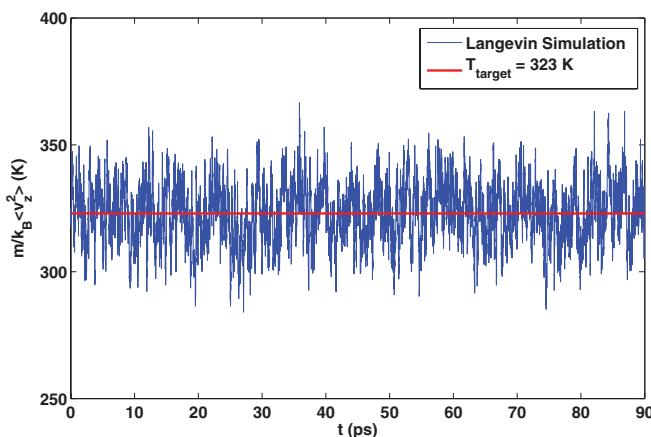


FIG. 3. Average temperature profile of the tracer particle during a Langevin simulation.

where, Δt is the time step, $F^{(1)}$ is the mean force ($-\frac{dW}{dz}$) evaluated at $z^{(1)}$ and η is a Gaussian random variable with zero mean and unit variance, sampled independently at each time step. The rest of the symbols have the same meaning as defined above. Since, these equations are time-irreversible equations, a small time step should be taken that ensures $\gamma \Delta t \ll 1$ to avoid artificial pumping of energy (increase in temperature) to the system. Further, the steepness of the PMF profile also requires that a very small time step be used for stable simulations. We used time steps in the range [0.001 – 0.01] ps for the systems considered in this work. After starting the simulation, initial 8–10 ps data was discarded before collecting the statistics. Figure 3 shows the temperature profile of the tracer particle (it is the same particle as the fluid molecules for self-diffusion) during the course of a Langevin simulation. All the results obtained for MSD and survival probability are computed by performing the averaging over 2500–3000 tracer particles. All MD simulations are performed using the simulation package GROMACS 3.3.1.¹⁷ To compare the MSD and the survival probabilities obtained from the model with those obtained from MD simulations, we used our earlier MD simulation data for confined carbon-dioxide,¹⁰ water,¹¹ and LJ fluids.⁹

IV. RESULTS

We use the model to compute the time evolution of MSD and survival probability of confined fluids in different interfacial layers. To compute static quantities such as equilibrium density, the assignment of a molecule to a particular layer can be unambiguously done based on its position alone, and is independent of the time. However, the assignment of a molecule for the computation of dynamic quantities such as MSD (or self-diffusion coefficient) is tricky as the molecule can move out of the layer during the sampling time. For computing dynamic quantities, two tagging strategies are generally used; (a) initial position based tagging in which a molecule is assigned to a layer if it is in the layer at the initial time t_0 , regardless of its position at subsequent times, (b) occupation-time based tagging in which a molecule is assigned to a particular layer only if it stays in that layer for certain percentile (say

60%) of the sampling time. The relative merits of these two approaches are discussed by Pinnick, Erramilli, and Wang.¹⁸ Here, we use the initial position based strategy to compute the MSD in different interfacial layers. Using this strategy, the MSD, $\langle [z(t) - z(t_0)]^2 \rangle$, is computed as

$$\langle [z(t) - z(t_0)]^2 \rangle = \frac{1}{J} \sum_{j=1}^J \frac{1}{N_j(t_0)} \sum_{i=1}^{N_j(t_0)} [z_i(t) - z_i(t_0)]^2, \quad (15)$$

where $z_i(t_0)$ is the position of a molecule at the starting time t_0 , $z_i(t)$ is its position at a later time t , and $N_j(t_0)$ is the number of particles present in the interfacial layer at time t_0 . The simulation time is partitioned into J blocks and this sampling process is repeated J times to perform block averaging. Survival probability is defined as the average probability that a particle which was inside a given layer at time t_0 still remains inside that layer at a later time t . For a region, $z_L \leq z \leq z_U$, the survival probability, $P([z_L, z_U], t; [z_L, z_U], t_0)$, can be defined as¹⁹

$$P([z_L, z_U], t; [z_L, z_U], t_0) = \int_{z_L}^{z_U} dz \int_{z_L}^{z_U} dz_0 P([z_L, z_U], t|[z_L, z_U], t_0) g(z_0), \quad (16)$$

where $P([z_L, z_U], t|[z_L, z_U], t_0)$ is the conditional probability that the particle was located in the region $z_L \leq z \leq z_U$ at time t , given that it was in the region $z_L \leq z \leq z_U$ at time t_0 . $g(z_0)$ is the probability for the particle to be in $z_L \leq z \leq z_U$ at time t_0 . In a particle based simulation, it is computed as

$$P([z_L, z_U], t; [z_L, z_U], t_0) = \frac{1}{J} \sum_{j=1}^J \frac{N_j(t)}{N_j(t_0)}, \quad (17)$$

where $N_j(t_0)$ is the number of particles present in the layer at time t_0 , and $N_j(t)$ is the number of those particles which still remain in the layer after time $t - t_0$. Survival probability is a domain length ($z_U - z_L$) dependent quantity and is used to determine the mean exit or escape time of a particle from the interfacial layer. Local translational mobility of the fluid molecules is also related to the average time a molecule spends in a given layer. We first use the model to compute the MSD and survival probability for carbon-dioxide ($m = 44$ amu) confined inside a 2.232 nm wide graphite slit. This is an ideal size system to test the model because it contains both an oscillatory density profile near the wall and a constant bulk-like density in the central region (see Fig. 4(a)) of the slit. The average density ρ_{avg} for this system is 9.0 molecules/nm³ and $\Delta \approx 0.27$ nm, which gives $\rho_{eff} \approx 11.9$ molecules/nm³. The self-diffusion coefficient D of bulk carbon-dioxide at density 11.9 molecules/nm³ and temperature 323 K is $\sim 16.5 \times 10^{-3}$ nm²/ps. Using this value of D in Eq. (12), we get $\gamma = 3.69$ ps⁻¹. These values are reported in Table I. The slit is divided into three interfacial regions (see Fig. 4(b)), that partition the molecules in layers, relative to their position from the wall. Figures 4(c) and 4(d) show the comparison of the MSD and survival probability in different regions, as computed from the model with those obtained from MD simulations. It can be observed that the predictions from the model (solid line) are in good agreement with those obtained from MD (broken line) simulations. Further, the MSD and survival

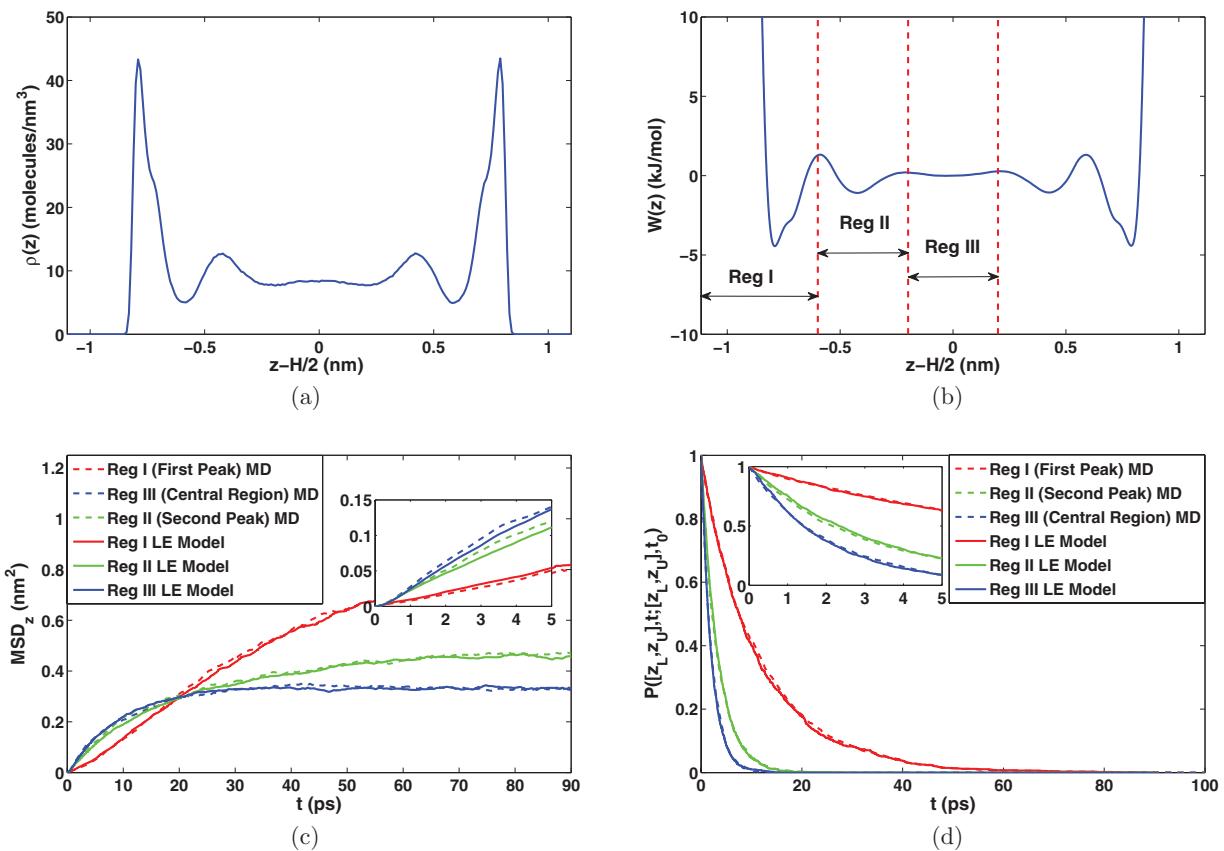


FIG. 4. (a) COM density Profile, $\rho(z)$, (b) PMF Profile, $W(z)$, (c) mean square displacement, MSD (inset: enlargement of MSD in 0–5 ps), (d) survival probability (inset: enlargement in 0–5 ps) of carbon-dioxide confined inside a $H = 2.232$ nm wide graphite slit. The average density, ρ_{avg} , is 9.0 molecules/nm³ and temperature is 323 K. Solid line represents the result from the combined Langevin-EQT (LE) model and dashed line is MD result.

probability can be used to estimate the local self-diffusion coefficient in different regions. The survival probability can be used to estimate the mean exit time, τ_z , for each region. It has been reported that the survival probability can be approximated, with high degree of accuracy, by an exponential decay of the form e^{-t/τ_z} .¹⁹ Once the mean exit time is computed, then the time evolution of the MSD in the range $[0, \tau_z]$ is fit to a linear polynomial and its slope (coefficient of the linear term) is used to compute the local self-diffusion coefficient. Table II shows the mean exit time and the local self-diffusion coefficient in the three regions. It can be observed that the self-diffusion coefficient of region I, which is closest to the wall, is significantly lower than that of regions II and III. Further, it can be said that unlike the motion in the direction parallel to the pore wall, for motion in the normal direction, it is the degree of structural inhomogeneity (or the depth of the potential well) that changes the average residence time of the

particle and results in different position-dependent transient behavior across the confinement.

Now, to check the performance of the model in strongly inhomogeneous systems, we compute the MSD and survival probability of carbon-dioxide confined inside 1.860 nm ($\rho_{avg} = 8.7$ molecules/nm³, $T = 348$ K) and 1.488 nm ($\rho_{avg} = 10$ molecules/nm³, $T = 323$ K) wide graphite slits. In these systems, the confinement makes the density profile inhomogeneous across the entire length of the slit (see Figs. 5(a) and 5(e)). The friction coefficient γ for these systems is reported in Table I. Figure 5 shows the average MSD and survival probability in different regions as predicted by the model for these two systems. It can be observed that for both systems, the predictions from the model are in reasonable agreement with those obtained from MD simulations. Though the results are physically consistent, there is a slight quantitative discrepancy in the predicted $MSDs$ and survival probabilities. Possible reason for this discrepancy could be the backscattering of the molecules (non-exponential decay of the velocity-ACF) at higher densities that gives rise to a slower collective dynamics. Further, for anisotropic molecules such as carbon-dioxide, under confinement, the shape of the molecule gives rise to an orientation dependent packing near the interface.¹⁰ This orientation dependent packing might result in a rotational motion, which we completely ignore by coarse-graining the molecule as a structureless spherical molecule placed at its COM position.

TABLE II. Mean exit time and self-diffusion coefficient in different regions^a for confined CO₂.

Region	Mean exit time, τ_z , (ps)	$D_z \times 10^{-3}$ nm ² /ps
Reg I	11.2	7.07
Reg II	3.4	12.55
Reg III	2.0	17.15

^aSee Fig. 4(b), System: $H = 2.232$ nm, $T = 323$ K, $\rho_{avg} = 9$ molecules/nm³.

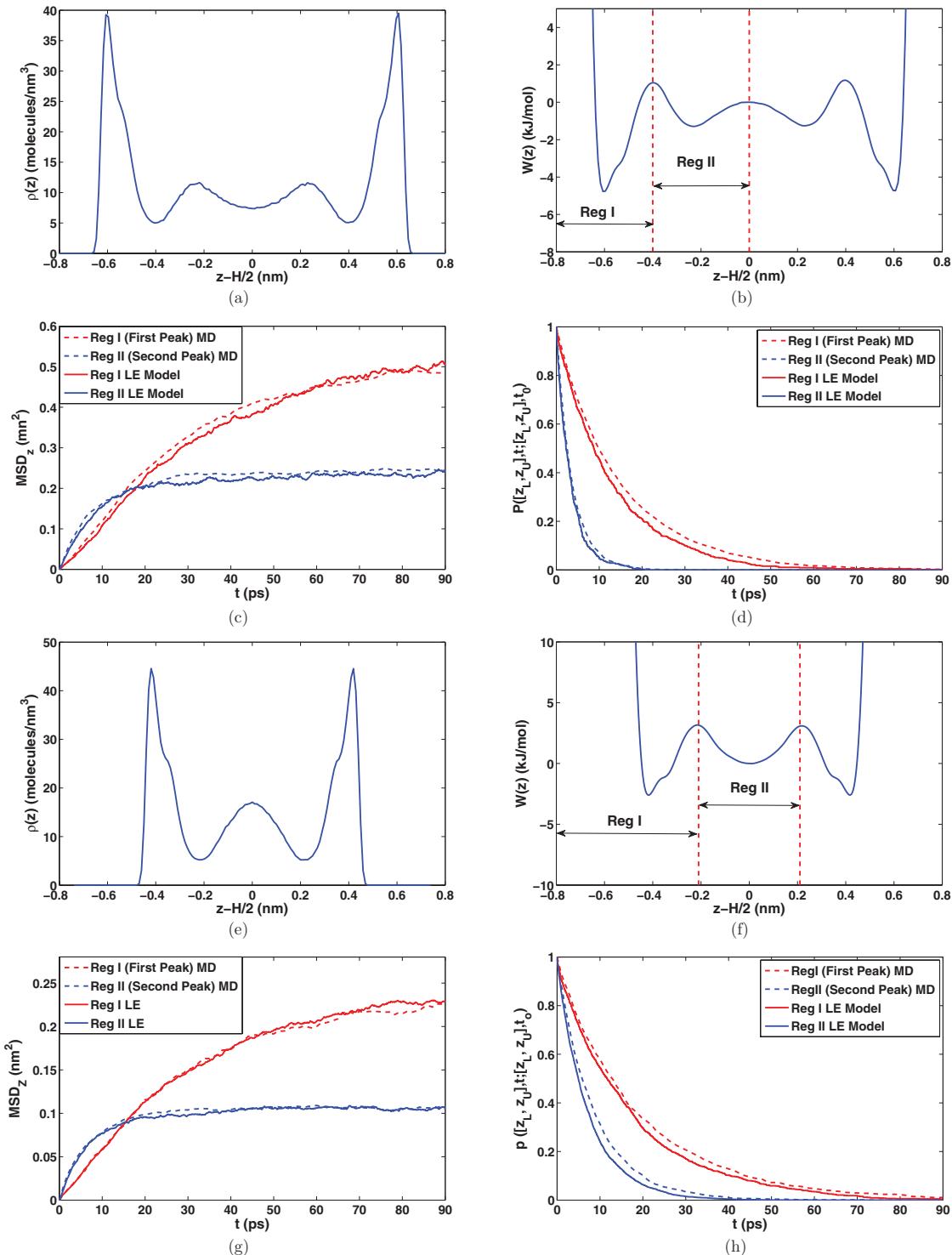


FIG. 5. (a)–(h) Comparison of MSD and survival probability of carbon-dioxide confined inside $H = 1.860 \text{ nm}$ ($\rho_{avg} = 8.7 \text{ molecules/nm}^3$, $T = 348 \text{ K}$) and $H = 1.488 \text{ nm}$ ($\rho_{avg} = 10 \text{ molecules/nm}^3$, $T = 323 \text{ K}$) wide graphite slits. Solid line represents the result from the combined Langevin-EQT (LE) model and dashed line is MD result. (a, e) COM density; (b, f) PMF; (c, g) MSD; and (d, h) Survival probability.

The development of noise models that can mimic thermally induced cooperative motion of bulk and confined fluids requires a more fundamental understanding, and is currently under progress. Further, we test the model to simulate the equilibrium dynamics of some other important fluids, and use it to predict the MSD and survival probability of SPC/E water ($m = 18 \text{ amu}$, $\rho_{avg} = 30 \text{ molecules/nm}^3$, $T = 300 \text{ K}$) and LJ argon ($m = 40 \text{ amu}$, $\rho_{avg} = 18.5 \text{ molecules/nm}^3$, $T = 300$

K) confined inside graphite slits. The friction coefficient γ for these systems is reported in Table I. It can be observed that the value of the friction coefficient for confined water system is quite large ($\gamma = 72.8 \text{ ps}^{-1}$), hence a time step Δt of 0.001 ps was used (to ensure $\gamma \Delta t \ll 1$ in Eq. (14b)) to simulate the system. Figures 6 and 7 show the comparison of the MSD and survival probability for these systems, as computed from the model with those obtained from MD simulations. It

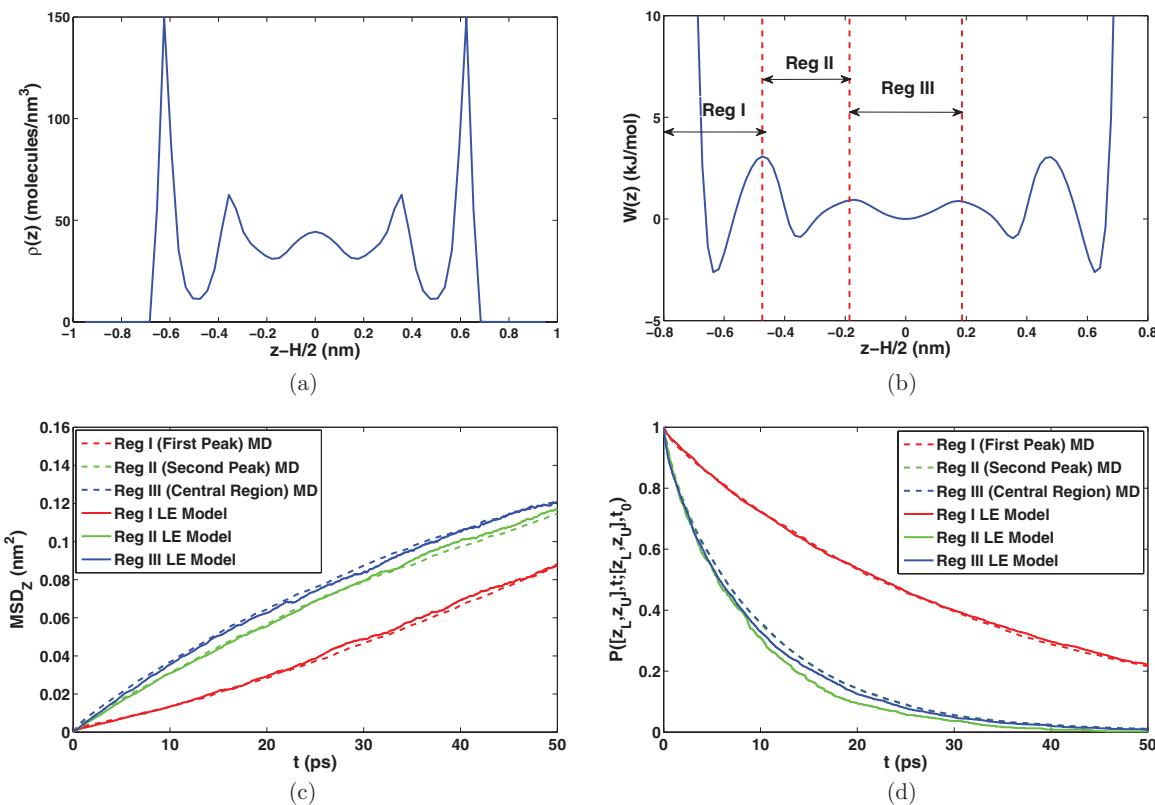


FIG. 6. (a)–(d) Comparison of MSD and survival probability of SPC/E water confined inside a $H = 1.902$ nm wide graphite slit with $\rho_{avg} = 30$ molecules/nm³ and $T = 300$ K. Solid line represents the result from the combined Langevin-EQT (LE) model and dashed line is MD result. (a) COM density; (b) PMF; (c) MSD; and (d) Survival probability.

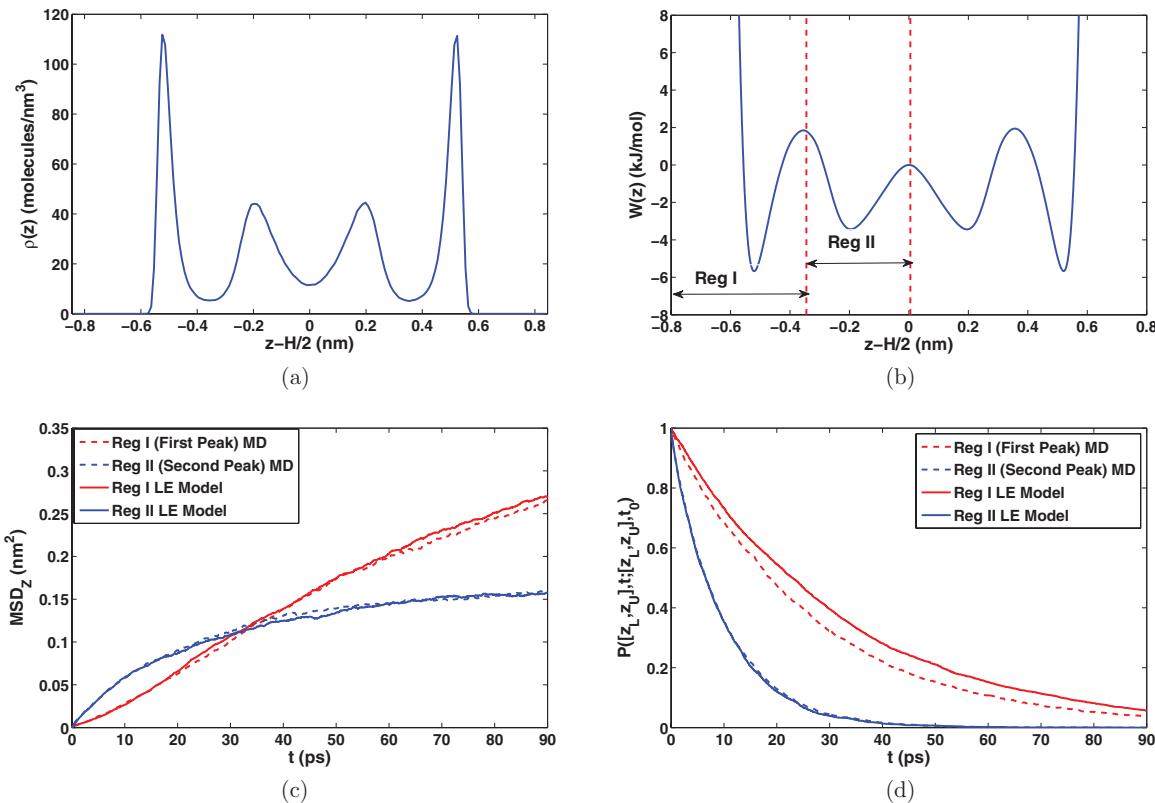


FIG. 7. (a)–(d) Comparison of MSD and survival probability of LJ argon confined inside a $H = 1.690$ nm wide graphite slit with $\rho_{avg} = 18.5$ molecules/nm³ and $T = 300$ K. Solid line represents the result from the combined Langevin-EQT (LE) model and dashed line is MD result. (a) Density; (b) PMF; (c) MSD; and (d) Survival probability.

can be observed that for confined water system, the predicted MSDs and survival probabilities (Figs. 6(c) and 6(d)) match reasonably well with those obtained from MD simulations. For confined argon system, though the MSDs (Fig. 7(c)) are in good agreement, there is a discrepancy between the predicted survival probability and MD survival probability (Fig. 7(d)) for region I. The model predicts a slower exit rate in comparison to that obtained from MD simulation. This discrepancy might be occurring because of the inability of the Langevin equation with delta correlated noise to predict the correct short-time dynamics in dense fluids. This short-time discrepancy is known to effect quantities that depend on the boundary.^{5,19} An indirect way to fix this short-time discrepancy is to shift the boundaries in the Langevin simulation such that the survival probability obtained from it matches with that obtained from MD simulation. It is discussed in Ref. 5.

V. CONCLUSIONS

In this work, we combine EQT with a phenomenological Langevin equation to simulate the equilibrium dynamics of confined fluids. The model is used to compute the MSD and survival probabilities of some important fluids such as carbon-dioxide, water, and LJ argon, confined inside graphite slits. The predictions from the model are found to be in agreement with those obtained from MD simulations. This approach provides a mathematically simple and computationally efficient means to study the impact of structural inhomogeneity on the self-diffusion dynamics of confined fluids.

ACKNOWLEDGMENTS

This work was supported by the AFOSR, and NSF under Grant Nos. 0328162 (nano-CEMMS, UIUC), 0852657, and

0915718. T. Sanghi wishes to thank Sikandar Mashayak for confined water data, and Kumar Kunal and Ravi Bhaduria for helpful discussions. The authors acknowledge the use of the Taub cluster provided by the Computational Science and Engineering Program at the University of Illinois.

- ¹H. T. Davis, I. Bitsanis, T. K. Vanderlick, and M. V. Tirrell, in *Supercomputer Research in Chemistry and Chemical Engineering*, edited by K. F. Jensen and D. G. Truhlar (American Chemical Society, 1987).
- ²H. T. Davis in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Marcel Dekker, Inc., New York, 1992).
- ³G. E. Karniadakis, A. Beskok, and N. R. Aluru, *Microflows and Nanoflows: Fundamentals and Simulation* (Springer Science+Business Media, Inc., New York, 2005), pp. 375–381.
- ⁴G. Goel, W. P. Kerkelberg, M. J. Pond, J. Mittal, V. K. Shen, J. R. Errington, and T. M. Truskett, *J. Stat. Mech.: Theory Exp.* **2009**, P04006.
- ⁵P. Liu, E. Harder, and B. J. Berne, *J. Phys. Chem. B* **108**, 6595 (2004).
- ⁶J. Mittal, T. M. Truskett, J. R. Errington, and G. Hummer, *Phys. Rev. Lett.* **100**, 145901 (2008).
- ⁷A. V. Raghunathan, J. H. Park, and N. R. Aluru, *J. Chem. Phys.* **127**, 174701 (2007).
- ⁸S. Chandrasekhar in *Selected Papers on Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, Inc., New York, 1954).
- ⁹T. Sanghi and N. R. Aluru, *J. Chem. Phys.* **132**, 044703 (2010).
- ¹⁰T. Sanghi and N. R. Aluru, *J. Chem. Phys.* **136**, 024102 (2012).
- ¹¹S. Mashayak and N. R. Aluru, *J. Chem. Theory Comput.* **8**, 1828 (2012).
- ¹²S. Mashayak and N. R. Aluru, *J. Chem. Phys.* **137**, 214707 (2012).
- ¹³R. Kubo, *Rep. Prog. Phys.* **29**, 255 (1966).
- ¹⁴R. Vogelsang and C. Hoheisel, *J. Stat. Phys.* **47**, 193 (1987).
- ¹⁵Z. Zhang and Z. Duan, *J. Chem. Phys.* **122**, 214507 (2005).
- ¹⁶T. Ladd, “Numerical methods for molecular and continuum dynamics,” see http://www.che.ufl.edu/ladd/publications/kmz_09.pdf.
- ¹⁷E. Lindahl, B. Hess, and D. van der Spoel, *J. Mol. Model.* **7**, 306 (2001).
- ¹⁸E. R. Pinnick, S. Erramilli, and F. Wang, *Mol. Phys.* **108**, 2027 (2010).
- ¹⁹P. J. Colmenares, F. Lopez, and W. Olivares-Rivas, *Phys. Rev. E* **80**, 061123 (2009).