

Supporting Information

Development of 3-dimensional time-dependent density functional theory and its application to gas diffusion in nanoporous materials

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Theoretical Details

1. Model

We consider the diffusion process of spherical molecule (guest) being adsorbed in a nanoporous material (host). The guest and the atoms of the host are modeled by spherical LJ12-6 potential:

$$u_{ij}(\mathbf{r}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad \backslash * \text{MERGEFORMAT (S1)}$$

where $u_{ij}(\mathbf{r})$ is the interaction potential between particle i and j , ε_{ij} and σ_{ij} are the well depth and diameter, which is parameterized by the universal force field (UFF) ¹ and mixing rule:

$$\begin{cases} \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \\ \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \end{cases} \quad \backslash * \text{MERGEFORMAT (S2)}$$

2. TDDFT

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The basic equation of TDDFT reads:

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \nabla \cdot \left(D \rho(\mathbf{r}, t) \nabla \frac{\delta \beta F}{\delta \rho(\mathbf{r}, t)} \right) \quad \text{* MERGEFORMAT (S3)}$$

To solve equation * MERGEFORMAT (S3), we have to know the expression of the free energy functional $F[\rho(\mathbf{r}, t)]$ firstly. Under the near equilibrium state approximation, the free energy functional of non-equilibrium state $F[\rho(\mathbf{r}, t)]$ can be approximated by the free energy of equilibrium state $F^{(0)}[\rho(\mathbf{r})]$:

$$F[\rho(\mathbf{r}, t)] \approx F^{(0)}[\rho(\mathbf{r})] \quad \text{* MERGEFORMAT (S4)}$$

Following the equilibrium DFT, $F^{(0)}[\rho(\mathbf{r})]$ can be separated into three terms: the idea free energy (id), the external free energy (ext) and the excess free energy (ex), representing the contribution from kinetic energy, adsorbent-adsorbate interaction and adsorbate-adsorbate correlation in our system, respectively:

$$F^{(0)}[\rho(\mathbf{r})] = F^{\text{id}}[\rho(\mathbf{r})] + F^{\text{ext}}[\rho(\mathbf{r})] + F^{\text{ex}}[\rho(\mathbf{r})] \quad \text{*}$$

MERGEFORMAT (S5)

The idea term can be exactly given by:

$$F^{\text{id}}[\rho(\mathbf{r})] = k_{\text{B}} T \int \rho(\mathbf{r}) [\ln \rho(\mathbf{r}) \Lambda^3 - 1] d\mathbf{r} \quad \text{* MERGEFORMAT}$$

(S6)

where $\Lambda = h / \sqrt{2\pi m k_{\text{B}} T}$ is the de Broglie wave length, h is the Planck constant and m is the mass of the molecule. Similar to idea term, the external term can also be expressed simply:

$$F^{\text{ext}}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) V^{\text{ext}}(\mathbf{r}) d\mathbf{r} \quad \text{* MERGEFORMAT (S7)}$$

where $V^{\text{ext}}(\mathbf{r})$ is the external potential, which is calculated by the summation of all host-guest interactions:

$$V^{\text{ext}}(\mathbf{r}) = \sum_{i \in \text{host}} u_{\text{guest},i}(\mathbf{r} - \mathbf{r}_i) \quad \backslash * \text{MERGEFORMAT (S8)}$$

where \mathbf{r}_i is the coordinate of atom i .

Generally, there is no exact expression for the excess free energy; and there are various method to approximate this term. In our previous work, we have demonstrated, that an approximation combining modified fundamental measure theory (MFMT), mean field theory (MFT) and weighted density approximation (WDA) works fairly well for gas adsorptions; and we implement this approximation in this work: First, the excess free energy is further separated into three terms:

$$F^{\text{ex}}[\rho(\mathbf{r})] = F^{\text{hs}}[\rho(\mathbf{r})] + F^{\text{attr}}[\rho(\mathbf{r})] + F^{\text{cor}}[\rho(\mathbf{r})] \quad \backslash *$$

MERGEFORMAT (S9)

where $F^{\text{hs}}[\rho(\mathbf{r})]$ is the hard sphere free energy functional representing repulsive contribution, which is approximated by the MFMT: ²

$$F^{\text{hs}}[\rho(\mathbf{r})] = k_{\text{B}}T \int \Phi[n_{\alpha}(\mathbf{r})] d\mathbf{r} \quad \alpha \in \{0, 1, 2, 3, \text{V1}, \text{V2}\} \quad \backslash *$$

MERGEFORMAT (S10)

where

$$\Phi[n^{(\alpha)}(\mathbf{r})] = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \mathbf{n}_{\text{V1}} \cdot \mathbf{n}_{\text{V2}}}{1 - n_3} + \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{36\pi n_3^2 (1 - n_3)^2} (n_2^3 - 3n_2 \mathbf{n}_{\text{V2}} \cdot \mathbf{n}_{\text{V2}})$$

* MERGEFORMAT (S11)

$$n_{\alpha}(\mathbf{r}) = \int \rho(\mathbf{r}') w^{(\alpha)}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \quad \alpha \in \{0, 1, 2, 3, \text{V1}, \text{V2}\} \quad \backslash *$$

MERGEFORMAT (S12)

$$\left\{ \begin{array}{l} w^{(2)}(r) = \pi d^2 w^{(0)}(r) = 2\pi d w^{(1)}(r) = \delta(d/2 - r) \\ w^{(3)}(r) = \theta(d/2 - r) \\ \mathbf{w}^{(\text{V2})}(\mathbf{r}) = 2\pi d \mathbf{w}^{(\text{V1})}(\mathbf{r}) = w^{(2)}(r) \frac{\mathbf{r}}{r} \end{array} \right. \quad \backslash *$$

MERGEFORMAT (S13)

where d is the hard sphere diameter. For LJ system, d can be determined by the Barker-

Henderson theory: ³

$$u^{\text{LJ}}(r) = u^{\text{hs}}(r) + u^{\text{attr}}(r) \quad \backslash* \text{ MERGEFORMAT (S14)}$$

$$u^{\text{hs}}(r) = \begin{cases} \infty & r < d \\ 0 & r > d \end{cases} \quad \backslash* \text{ MERGEFORMAT (S15)}$$

$$u^{\text{attr}}(r) = \begin{cases} 0 & r < \sigma \\ 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & r > \sigma \end{cases} \quad \backslash* \text{ MERGEFORMAT}$$

(S16)

$$d = \frac{1 + 0.2977(\beta\varepsilon)^{-1}}{1 + 0.33163(\beta\varepsilon)^{-1} + 0.0010477(\beta\varepsilon)^{-2}} \sigma \quad \backslash*$$

MERGEFORMAT (S17)

$F^{\text{attr}}[\rho(\mathbf{r})]$ is the attractive free energy functional, which is approximated by the MFT:

$$F^{\text{attr}} = \frac{1}{2} \iint \rho(\mathbf{r}) \rho(\mathbf{r}') u^{\text{attr}}(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad \backslash* \text{ MERGEFORMAT}$$

(S18)

$F^{\text{cor}}[\rho(\mathbf{r})]$ is the correlation free energy functional, which is determined by WDA:

$$F^{\text{cor}} = \int \rho(\mathbf{r}) f^{\text{cor}}[\bar{\rho}(\mathbf{r})] d\mathbf{r} \quad \backslash* \text{ MERGEFORMAT (S19)}$$

where $\bar{\rho}(\mathbf{r})$ is the weighted density, which is defined by:

$$\bar{\rho}(\mathbf{r}, t) = \frac{3}{4\pi\sigma^3} \int \rho(\mathbf{r}', t) \Theta(|\mathbf{r} - \mathbf{r}'| - \sigma) d\mathbf{r}' \quad \backslash* \text{ MERGEFORMAT}$$

(S20)

f^{cor} is the correlation free energy density of homogeneous fluid, which is given by:

$$f^{\text{cor}}(\rho) = \frac{F_{\text{bulk}}^{\text{LJ}}(\rho)}{N} - \frac{F_{\text{bulk}}^{\text{hs}}(\rho)}{N} - \frac{F_{\text{bulk}}^{\text{MFA}}(\rho)}{N} \quad \backslash* \text{ MERGEFORMAT}$$

(S21)

where $F_{\text{bulk}}^{\text{LJ}}(\rho)$ and $F_{\text{bulk}}^{\text{hs}}(\rho)$ are the free energy of bulk LJ fluids and bulk hard sphere fluids, respectively, while $F_{\text{bulk}}^{\text{MFA}}(\rho)$ is the attractive free energy for bulk fluids, which can be generated at the bulk limit of equation * MERGEFORMAT (S18):

$$\frac{F_{\text{bulk}}^{\text{MFA}}(\rho)}{N} = -\frac{16}{9}\pi\beta\varepsilon\rho\sigma^3 \quad \text{* MERGEFORMAT (S22)}$$

The expressions for $F_{\text{bulk}}^{\text{LJ}}(\rho)$ and $F_{\text{bulk}}^{\text{hs}}(\rho)$ can be formulated by the corresponding equation of state (EOS): For $F_{\text{bulk}}^{\text{LJ}}(\rho)$, the MBWR EOS is employed: ⁴

$$\frac{F_{\text{bulk}}^{\text{LJ}}(\rho)}{N} = \varepsilon \left(\sum_{i=1}^8 \frac{a_i \rho^i \sigma^{3i}}{i} + \sum_{i=1}^6 b_i G_i \right) \quad \text{* MERGEFORMAT (S23)}$$

where the detailed expression for a_i , b_i and G_i can be found in the literature. ⁴ For $F_{\text{bulk}}^{\text{hs}}(\rho)$, the Carnahan-Starling (CS) EOS is employed: ⁵

$$\frac{F_{\text{bulk}}^{\text{hs}}(\rho)}{N} = k_{\text{B}} T \frac{4\eta - 3\eta^2}{(1-\eta)^2} \quad \text{* MERGEFORMAT (S24)}$$

where $\eta = \pi\rho d^3 / 6$.

From equations * MERGEFORMAT (S4) ~ * MERGEFORMAT (S24), we can formulate the free energy functional $F[\rho(\mathbf{r}, t)]$; and equation * MERGEFORMAT (S3) can be solved numerically. To accelerate the calculation, the fast Fourier transform (FFTW package ⁶) is used to compute all convolutions (such as equation * MERGEFORMAT (S12), * MERGEFORMAT (S18) and * MERGEFORMAT (S20)):

$$\int f_1(\mathbf{r}) f_2(\mathbf{r}-\mathbf{r}') d\mathbf{r}' = F^{-1} \{ F[f_1(\mathbf{r})] F[f_2(\mathbf{r})] \} \quad \text{* MERGEFORMAT (S25)}$$

MERGEFORMAT (S25)

where F and F^{-1} stand for the forward and backward Fourier transforms,

respectively. The derivatives presented in equation * MERGEFORMAT (S3) are calculated by numerical differences with step length 0.05 nm and 0.1 fs for \mathbf{r} and t , respectively. The cutoff distance for LJ potential is 1.3 nm. The external potential $V^{\text{ext}}(\mathbf{r})$, correlation free energy density $f^{\text{cor}}(\rho)$ and density dependent diffusion $D(\rho)$ (equation (3) in the main text) are pre-tabulated before the TDDFT iteration.

References:

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