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Excess-entropy scaling of dynamics for methane in various nanoporous materials

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ABSTRACT

Molecular simulation was conducted to test the validity of two excess entropy scaling laws proposed by Rosenfeld and Dzugutov for extending their use in describing the diffusion of CH_4 molecules through zeolites and metal–organic frameworks. The functional relationships between self-diffusivity and excess entropy formulated by the two laws are found to hold with the modified pre-exponential scaling parameters. Based on this finding, new relations for the two scaling laws are proposed for predicting the diffusivities of CH_4 molecules in nanoporous materials within a wide range of concentrations and temperature conditions.

1. Introduction

A wide variety of nanoporous materials such as zeolites, metal–organic frameworks (MOFs), and silica nanopores are used for adsorptive and membrane separations and catalysis [1–3]. For an appropriate design of both the materials and related processes, the diffusion of guest molecules through the host structure of these nanoporous materials must be understood. However, in the past few years, predicting the influence of confinement on transport properties can be a challenging task [4–6].

In studying atomic and molecular diffusion in bulk Lennard–Jones (LJ) fluids, two excess entropy scaling laws by Rosenfeld [7] and Dzugutov [8] have been found to predict diffusivity in bulk simple fluids [9]. The two laws are identical in dimensionless form, i.e.,

$$D_s^* = A\exp(-Bs^{ex}) \tag{1}$$

where D_s^* and s^{ex} denote the reduced self-diffusivity and excess entropy, respectively; A is the pre-exponential scaling parameter; and B is a parameter that weakly depends on species [10]. In Table 1, the definitions of D_s^* and the values of A and B are given for equilibrium bulk LJ liquids. The remarkable features of the two scaling laws lie in the connection among the dynamic quantity, diffusivity, and the experimentally or numerically accessible thermodynamic quantity, s^{ex} [8]. Many researchers [11–15] have examined the two scaling laws by performing molecular simulations and illustrated that the reduced self-diffusivity both of bulk and confined fluids (atomic or molecular fluid) collapses onto a common curve when plotted against the excess entropy.

For the extension of the excess-entropy scaling to confined fluids, He et al. [16] have examined the prospect of using excess entropy scaling laws to describe the dynamics of CH_4 molecules through simple silica pore structures. It is found that the functional relationships between self-diffusivity and excess entropy formulated by the two laws are found to hold with the pre-exponential scaling parameters being peculiarly scale dependent. Studying the dynamics for monatomic sorbates confined within NaY zeolite, Borah et al. [17] have found that a suitably scaled dimensionless self-diffusivity shows an exponential dependence on the excess entropy of the adsorbed phase. Recently, Liu et al. [18] have presented an efficient computational procedure for the rapid prediction of the self-diffusivity of gas molecules in nanoporous materials by a combination of the Knudsen model, Rosenfeld scaling method, and a classical density functional theory (DFT). The self-diffusivity conforms to the Knudsen model at low density, and the effects of intermolecular interactions at higher densities are accounted for by Rosenfeld scaling method.

In this Letter, we explore the possibility of extending the Rosenfeld [7] and Dzugutov [8] scaling laws for their use in the diffusion of methane in zeolites and MOFs, each with its own diffusion behavior. We study the diffusion of simple CH_4 molecules through zeolites and MOFs by implementing Molecular Dynamic (MD) simulations to yield the self-diffusivity data and grand-canonical transition-matrix Monte Carlo (GC-TMMC) simulations of the excess entropy per CH_4 molecule. Our results extend the use of the two scaling laws originating from bulk fluids for evaluating single-component diffusion coefficients in real nanoporous materials, such as zeolites and MOFs.

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Table 1
Parameters for the two excess entropy scaling laws of bulk LJ fluids [7,8].

Scaling laws	A	B	D_s^*
Rosenfeld [27]	0.580	0.79	$= D_s\rho^{1/3}[m/k_BT]^{1/2}$ [a]
Dzugutov [28]	0.078	1.00	$= D_s\rho^{2/3}\Gamma_E^{-1}$ [b]

[a] ρ Is the number density, k_B is the Boltzmann constant, T is temperature, and m is the particle mass.

[b] $\Gamma_E = 4\pi\sigma^2\rho g(\sigma)(k_BT\pi m)^{1/2}$ is the effective Enskog interparticle collision frequency relevant to the microscopic molecular-level processes. σ is the inter-particle separation corresponding to the first peak in the radial distribution function, and $g(\sigma)$ is the magnitude of the peak.

2. Molecular models and simulation methods

2.1. Nanopore materials structures

In this Letter, we attempted to broaden our set of zeolites and MOFs as much as possible by selecting six widely varying topologies. The unit cell data are summarized in Table 2.

2.1.1. Channel-type zeolites

The class of channel-type zeolites is very diverse. All zeolites with diffusion occurring only in one direction, i.e., in straight channels that are not interconnected, fall under this category. Thus, channel-type zeolites can consist of one-dimensionally connected cages. To gain insight into the diffusion behavior of this class, we focus on one channel-type AFI zeolite comprising straight channels that are not interconnected. Diffusion occurs only in the z-direction. A unit cell of AFI contains two channels [19].

2.1.2. Intersecting channel-type zeolites

In this Letter, we examine one intersecting channel structure: MFI-type zeolites whose unit cell structures are depicted in Ref. [20]. For intersecting channel-type zeolites, considering 'cage' widths and window-to-cage ratios is impractical. The widest parts of the channels are usually regions where such channels are intersected by a perpendicular channel. This type consists of straight 10-ring channels running in the y-direction and intersected by so-called zigzag channels that run in the x and z-directions also consisting of 10-membered ring windows.

2.1.3. Three-dimensional cage-type zeolites

In this Letter, we consider FAU zeolite that has a three-dimensional pore structure with pores running perpendicular to one another in the x-, y-, and z-planes. Such zeolite is made of secondary building units 4, 6, and 6–6. The pore diameter is large at 7.4 Å because the aperture is defined by a 12-member oxygen ring that results in a larger cavity 12 Å in diameter. The cavity is surrounded by 10 sodalite cages (truncated octahedra) connected on their hexagonal faces [20].

Table 2
Simulation data of four zeolites and two MOFs.

Species	Unit cell dimension (Å)			Unit-cell type	Simulation box
	a	b	c		
AFI	23.774	13.726	8.484	Orthorhombic	$2\times2\times4$
MFI	20.022	19.899	13.383	Orthorhombic	$2\times2\times4$
FAU	25.028	25.028	25.028	Cubic	$1\times1\times1$
MCM-22	24.447	14.115	24.882	Orthorhombic	$2\times4\times2$
IRMOF-1	25.832	25.832	25.832	Orthorhombic	$1\times1\times1$
Na-*rho*-ZMOF	31.062	31.062	31.062	Orthorhombic	$1\times1\times1$

2.1.4. Different independent pore system zeolites

Zeolite MCM-22 (IZA structure code MWW) is unique in its framework topology because it has two independent pore systems [21]. One pore system consists of two-dimensional sinusoidal intersecting channels with elliptical 10-member ring cross-sections (4.1×5.1 Å). The other system possesses large cylindrical supercages with a diameter defined by a 12-MR (7.1 Å) and a height of 18.2 Å. These supercages are accessible through 10-MR apertures (4.0×5.5 Å).

2.1.5. MOFs

We adopted the structure of *rho*-ZMOF taken from the experimental work of Liu et al. [22] and dealt with the structure in its dehydrated form free of residual water molecules [22]. Rho-ZMOF possesses a 4-connected MOF resembling the topology of its counterpart zeolite RHO, with the space group being Im3 m with $a = b = c = 31.062$ Å. More details of the structural chemistry characteristics of *rho*-ZMOF can be found in literature [22] and are thus not repeated here.

IRMOF-1 is an isoreticular MOF and is also known as MOF-5 [23]. MOF-5 has a lattice constant of 25.832 Å, a crystal density of 0.593 g/cm^3, a free volume of 79.2%, and a surface area of 2833 m^2/g. For simulation, the atomic coordinates within the crystal were constructed using experimental X-ray crystallographic data [23].

2.2. Methane structure and potential parameters

CH_4 was selected as the guest diffusing molecule represented by a united-atom model with the 12–6 LJ potential [24]. The potential parameters (σ and ε) for CH_4 and zeolites were adopted from Dubbeldam et al. [24], as listed in Table 3. The parameters for Na-*rho*-ZMOF and IRMOF-1 materials listed in Table 3 were taken from Babarao et al. [25]

2.3. MD and GC-TMMC Simulation methods

We performed MD and GC-TMMC simulations to acquire dynamic and thermodynamic data within the range of state conditions from 300 K to 700 K and $0.01 < c < 0.05$ molecules/Å^3, where c is the pore concentration of CH_4 in terms of molecules per accessible pore volume. For all simulations, the simulation box sizes for the various simulated systems are given in Table 2. The simulated system was kept in a canonical ensemble with a Nose–Hoover thermostat, and the equations of motion were integrated using a sixth-order Gear predictor–corrector algorithm [26] embodied in the MUSIC program [27]. Simulation runs were performed with a cutoff distance of 14 Å for non-bonded interactions. The runs were conducted for a total period of 10.0 ns with

Table 3
LJ parameters for CH_4, zeolites, IRMOF-1 and Na-ρ-ZMOF materials.

Species	σ (Å)	ε/k_B (K)
O_z [a]	3.470	115.000
CH_4	3.73	148.000
C	3.430	52.851
H	2.571	22.147
O	3.118	30.200
N	3.261	34.731
In	3.976	301.505
Zn	2.462	62.393
Na^+	2.658	15.090

[a] O_z are the oxygens of the zeolites. LJ interactions between Si and CH_4 are not taken into account. Interaction parameters for non-identical groups are calculated using the Jorgensen mixing rules [2].