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Short Communication

A rationalization of the Type IV loading dependence in the Kärger–Pfeifer classification of self-diffusivities

Rajamani Krishna [a,b,*], Jasper M. van Baten [a]

[a] Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
[b] Department of Chemical & Biomolecular Engineering, University of California–Berkeley, CA 94720, USA

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ABSTRACT

Kärger and Pfeifer (1987) [1] have listed five different types of dependencies of the self-diffusivities, $D_{i,\mathrm{self}}$, on the loading, Θ_i, of guest molecules in zeolites. Of these five types, the Type IV dependence is particularly intriguing because it displays a maximum in the $D_{i,\mathrm{self}} - \Theta_i$ dependence for FAU zeolite. On the basis of published experimental data, and molecular simulations, for a variety of guest–host combinations we present arguments to suggest that the reasons for the curious maximum can be traced to molecular clustering. The clustering can be caused due to hydrogen bonding effects as is the case for methanol diffusion in NaY, or due to the temperatures being lower than the critical temperature, T_c.

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1. Introduction

In an influential review published in 1987 in the forerunner to this Journal, Kärger and Pfeifer [1] have listed five different types of dependencies of the self-diffusivities, $D_{i,\mathrm{self}}$, on the loading, Θ_i, of guest molecules in different zeolites. Of these five types, the Type IV dependence is particularly intriguing because it displays a maximum in the $D_{i,\mathrm{self}} - \Theta_i$ dependence for medium pore size FAU zeolite; see the data in Fig. 1a for self-diffusivity of acetonitrile in NaX zeolite at 393 K, and 485 K, re-plotted using the information provided by Kärger and Pfeifer [1]. The observed behaviors in Fig. 1a are rather abnormal, because for open structures such as NaX and NaY, with window sizes of about 7.4 Å, we should normally expect a monotonic decrease in the self-diffusivity with increased loading of the guest molecules [2–5]. Brandani et al. [6] have also reported Type IV loading dependence for methanol diffusion in NaX at 373 K; see Fig. 1b. More recently, Déroche et al. [7] have published QENS data for CH_4 diffusion in NaY at 200 K; see Fig. 1c. Their data indicate Type IV behavior at 200 K, but earlier published information for diffusion of CH_4 in NaX and NaY zeolites at higher temperatures, no such Type IV behavior is observed [8,9]. The Type IV loading dependence is not restricted to NaX, and NaY zeolites, and has also been reported by Valiullin et al. [10] for cyclohexane diffusion in mesoporous Vycor glass; see Fig. 1d.

The objective of this note is to provide a molecular level explanation for the Type IV loading dependence. We trace the origin of this behavior to molecular clustering.

2. Molecular clustering

In several recent publications the influence of molecular clustering on the diffusion characteristics of a guest molecules in micro- and mesoporous host structures, with pore sizes larger than 0.74 nm, have been highlighted [11–16]. There are two main reasons for molecular clustering.

Firstly, clustering of guest molecules within micro- and mesoporous materials can be initiated when the temperature T approaches, or falls below, the critical temperature, T_c. At sub-critical temperatures we have a meta-stable thermodynamic state within the pores [11]. One characteristic signature of this meta-stability is that the inverse thermodynamic factor, defined by

$$\frac{1}{\Gamma_i} \equiv \frac{\partial \ln \Theta_i}{\partial \ln f_i} = \frac{f_i}{\Theta_i}\frac{\partial \Theta_i}{\partial f_i} \tag{1}$$

has values exceeding unity for a range of molecular loadings, Θ_i. To appreciate the concept of molecular clustering, it is best to first discuss the simple case for which the adsorbed phase concentration follows a single-site Langmuir isotherm

$$\Theta_i = \Theta_{i,\mathrm{sat}} \frac{b_i f_i}{1 + b_i f_i} \tag{2}$$

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* Corresponding author at: Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands. Tel.: +31 20 6270990; fax: +31 20 5255604.

E-mail address: r.krishna@uva.nl (R. Krishna).

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Notation

b_i	Langmuir adsorption constant for species i, Pa^{-1}
$D_{i,\mathrm{self}}$	self-diffusivity of species i, $\mathrm{m^2\,s^{-1}}$
f_i	fluid phase fugacity of species i, Pa
T	absolute temperature, K
T_c	critical temperature, K

Greek letters

Γ_i	thermodynamic factor, dimensionless
θ_i	fractional adsorbate coverage of species i, dimensionless
Θ_i	loading of i, molecules per cage or unit cell
$\Theta_{i,\mathrm{sat}}$	saturation loading of i, molecules per cage or unit cell

Differentiation of Eq. (2) yields

$$\frac{1}{\Gamma_i} = 1 - \theta_i \tag{3}$$

where we define the fractional *occupancies*, θ_i

$$\theta_i \equiv \Theta_i / \Theta_{i,\mathrm{sat}} \tag{4}$$

Eq. (3) shows that inverse thermodynamic factor, $1/\Gamma_i$, equals the fractional *vacancy* $(1-\theta_i)$ for a Langmuirian adsorbed phase, and in this case we must have $1/\Gamma_i \leqslant 1$.

Let us consider the loading dependence of $1/\Gamma_i$ for CH_4 adsorption in NaY at T = 150 K, 180 K, 190 K, 200 K, and 300 K, determined from Configurational-Bias Monte Carlo (CBMC) simulations [11,12]; see Fig. 2a. The critical temperature of CH_4 is 191 K. We note that as the temperatures fall increasingly below 300 K, there is a region of pore loadings Θ_i for which $1/\Gamma_i > 1$. In these regions the fractional vacancy, as defined for a Langmuirian adsorbed phase by Eq. (3) exceeds unity. The physical interpretation of this situation is that in the actual case there is a certain degree of molecular clustering, as has been explained in detail in our earlier works [11,12]. A molecular cluster can be regarded as a k-mer. A k-mer occupies the same vacant adsorbed site as a normal, unclustered, molecule. As a consequence, it is feasible to have the fractional vacancy exceed unity, i.e. $1/\Gamma_i > 1$. To illustrate this pictorially, consider a square lattice containing 64 adsorption sites; see Fig. 3a. If the molecular species, 10 in total, are all unclustered the fractional occupancy is $\theta_i = 10/64$, and the fractional vacancy $1-\theta_i = 54/64$. If clustering occurs and dimers are formed, the

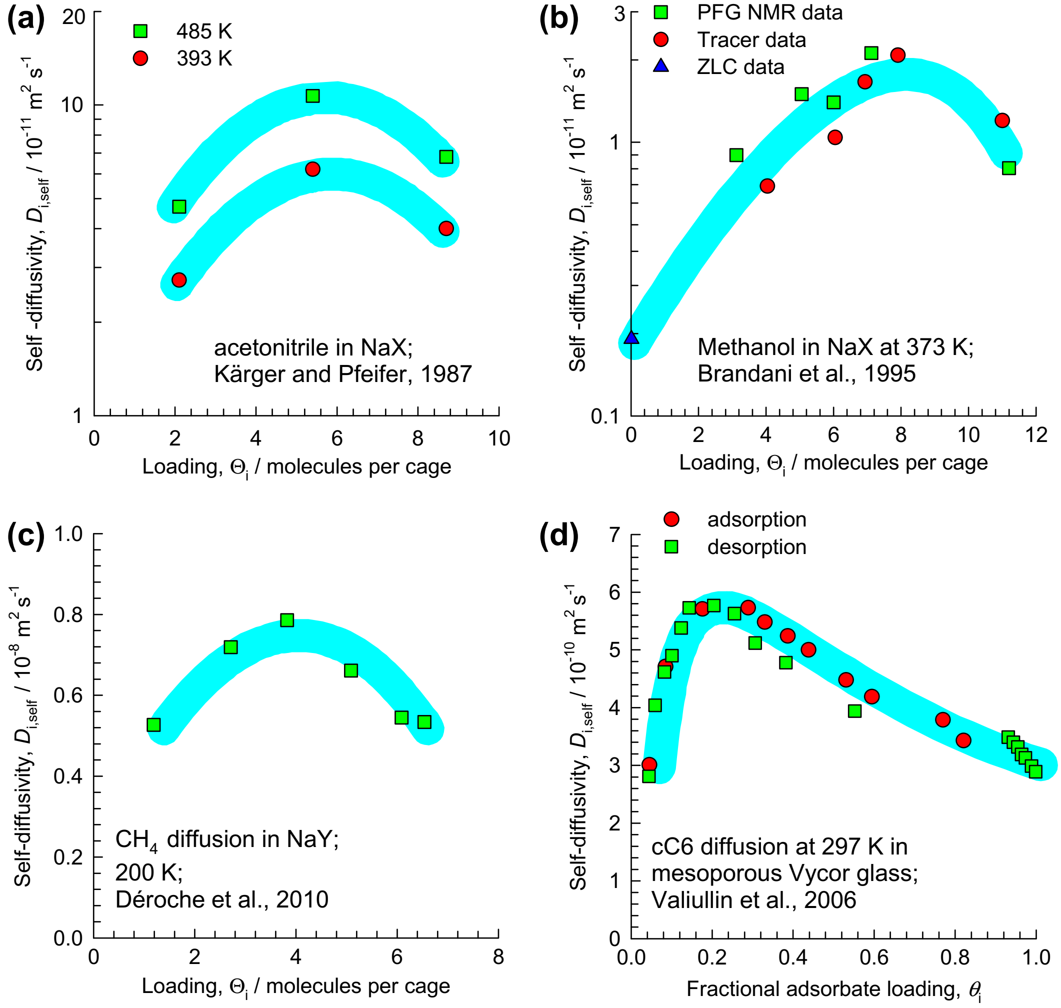

Fig. 1. Published experimental data for the loading dependence of self-diffusivities, $D_{i,\mathrm{self}}$ for various guest–host structures. (a) Acetonitrile in NaX at 393 K and 485 K [1], (b) methanol in NaX at 373 K [6], (c) CH_4 in NaY at 200 K [7], and (d) cyclohexane in Vycor glass at 297 K [10].

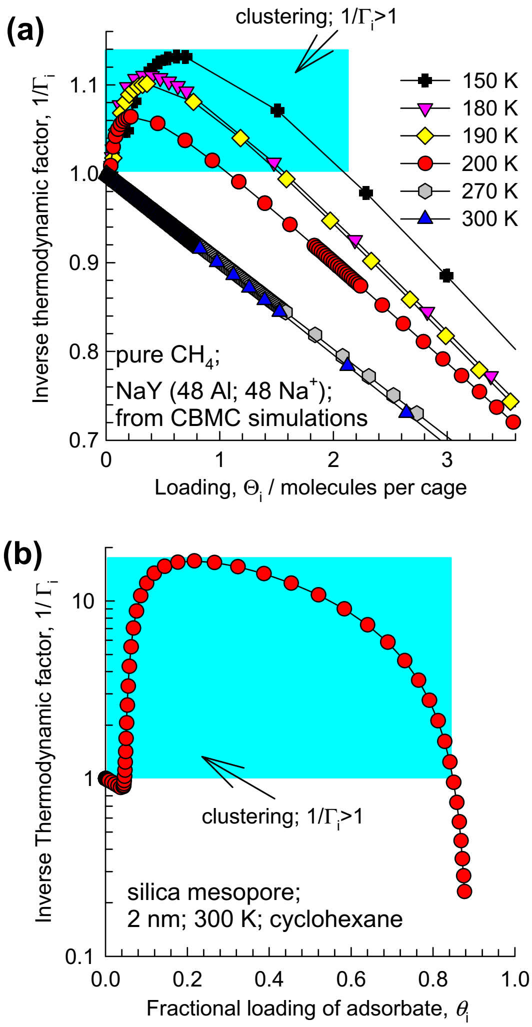

Fig. 2. The inverse thermodynamic factor, $1/\Gamma_i$, plotted as a function of the pore loading, Θ_i, for (a) CH_4 adsorption in NaY at a variety of temperatures [11,12] and (b) cyclohexane adsorption in a 2 nm silica mesopore at 300 K [16]. The animations in Videos 1 and 2 give a qualitative indication of the clustering phenomena for cyclohexane in a 2 nm silica mesopore.

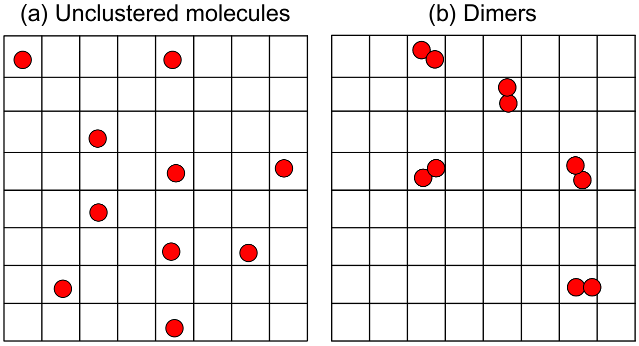

Fig. 3. (a) Adsorption of 10 unclustered molecular species on a square lattice containing 64 adsorption sites. (b) Adsorption of dimers.

same number of molecules will occupy only five sites; see Fig. 3b. The remaining number of vacant locations, 59, are still available for occupation. Even if no more clusters are formed, this would imply that a total of 10 + 59 = 69 molecules could be accommodated on the square lattice. Cluster formation has the effect of increasing the fractional vacancy $1 - \theta_i$ to the value of 59/54. For this reason it is possible to have $1/\Gamma_i > 1$ when clustering occurs. Conversely, the occurrence of $1/\Gamma_i > 1$ can be taken to imply the existence of molecular clusters. The motion of *k*-mers has a different characteristic than is the case for unclustered molecules. The motion of clusters may cause the diffusivity to increase for a range of loadings because the hopping from one vacant site to another occurs in a "concerted" fashion. The net result is that, for the range of loadings in which $1/\Gamma_i > 1$, we may expect the diffusivities to display a maximum, as observed in the QENS data of Déroche et al. [7]. For $T \gg T_c$, no such maximum is detected [8,9].

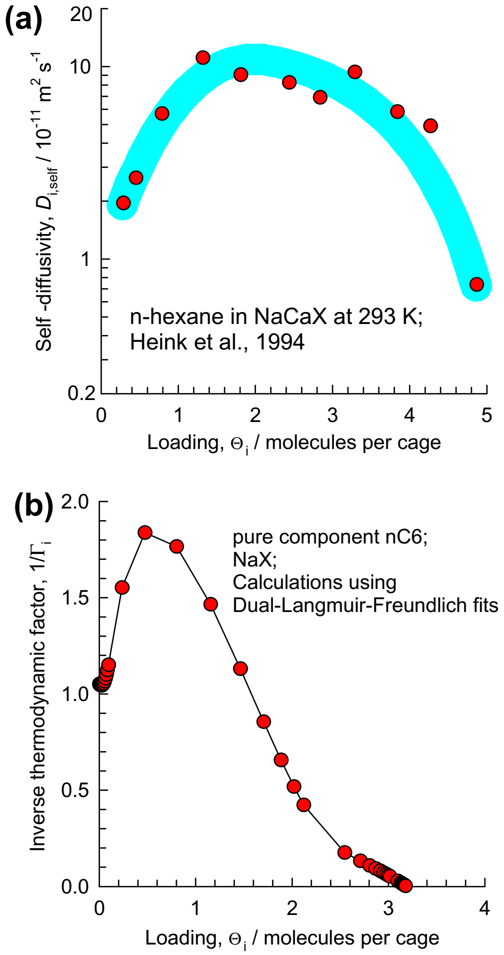

Fig. 4. (a) PFG NMR experimental data of Heink et al. [19] for self-diffusivity, $D_{i,\mathrm{self}}$, of *n*-hexane (nC6) in NaCaX at 293 K. The data are for 75 Ca atoms. (b) The inverse thermodynamic factor, $1/\Gamma_i$, plotted as a function of the pore loading, Θ_i, for nC6 adsorption in NaX at 293 K.

The critical temperature of acetonitrile is 545 K, significantly higher than the two temperatures at which Type IV behavior is observed by Kärger and Pfeifer [1] for diffusion in NaX, suggesting that molecular clustering is the root cause.

For cyclohexane, T_c = 553 K, and for diffusion at ambient temperature conditions inside mesopores we may expect a significant degree of molecular clustering [16]. As illustration, Fig. 2b shows the data on $1/\Gamma_i$ for a 2 nm silica mesopore at 300 K, obtained from CBMC simulations. We note that $1/\Gamma_i \gg 1$ for a wide range of adsorbate occupancies. The maximum in the self-diffusivity reported by Valiullin et al. [10] for diffusion of cyclohexane (cC6) at 297 K in mesoporous Vycor glass is directly attributable to increase in the inverse thermodynamic factor above unity values for the corresponding values of θ_i.

For alkanes, T_c increases with increasing chain length: ethane (C2, $T_c = 305$ K), propane (C3, $T_c = 370$ K), *n*-butane (nC4, $T_c = 425$ K), *n*-pentane (nC5, $T_c = 470$ K), *n*-hexane (nC6, $T_c = 507.4$ K), and *n*-heptane (nC7, $T_c = 540$ K). For a fixed temperature of 300 K the degree of clustering increases with increasing chain length. This explains the Type IV loading dependence observed for self-diffusivity of higher alkanes in CuBTC [17,18], a metal–organic framework with a open structure similar to FAU zeolite. Fig. 4a shows the PFG NMR experimental data of Heink et al. [19] for self-diffusivity, $D_{i,\text{self}}$, of *n*-hexane (nC6) in NaCaX at 293 K, well below the critical temperature of 507.4 K. We should therefore expect a significant degree of clustering of nC6 molecules and this is the most likely reason for the Type IV behavior. To verify that clustering does indeed occur, we undertook CBMC simulations to determine the inverse thermodynamic factor for nC6 in NaX at 293 K; these data are shown in Fig. 4b. It can be seen that $1/\Gamma_i > 1$ for the range of loading 0.0–1.5 molecules per cage, confirming the phenomenon of molecular clustering.

The second reason why clustering manifests within pores larger than 0.74 nm is due to hydrogen bonding. Hydrogen bonding manifests for guest molecules such as water and alcohols [13–15]. As illustration, Fig. 5a presents the CBMC simulation results for $1/\Gamma_i$ for methanol and ethanol adsorption in all-silica FAU at $T = 300$ K. For a wide range of loadings Θ_i for which $1/\Gamma_i > 1$, and we should expect Type IV behavior in these regions. Molecular dynamics (MD) simulations [13–15] for self-diffusion in FAU confirm these expectations; see Fig. 5b. The data in Fig. 5 provide a rationale for the Type IV behavior observed for methanol diffusion in NaX [6].

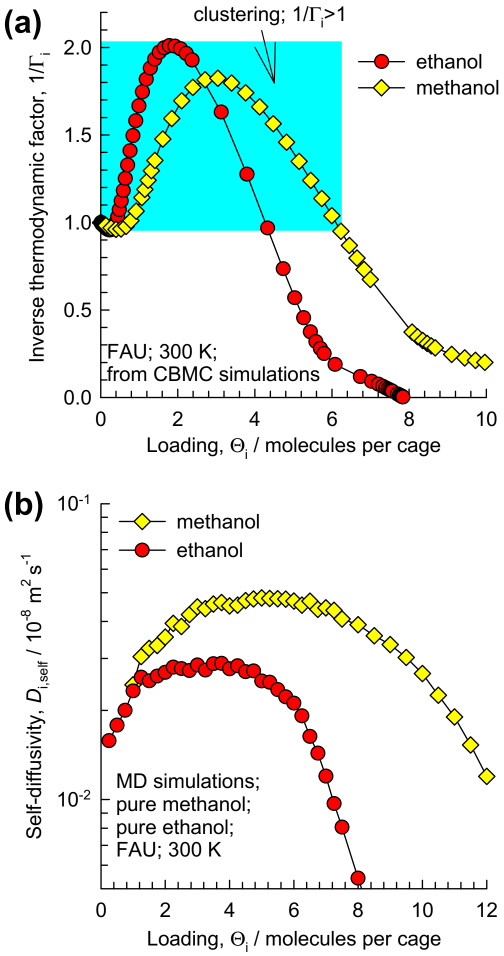

Fig. 5. (a) The inverse thermodynamic factor, $1/\Gamma_i$, plotted as a function of the pore loading, Θ_i, for (a) methanol and ethanol adsorption in FAU at 300 K (b) MD simulations for $D_{i,\text{self}}$ for methanol and ethanol diffusion in FAU at 300 K [16]. A qualitative appreciation of clustering of methanol and ethanol can be obtained by viewing Videos 3 and 4, provided as Supplementary material accompanying this publication.

Jost et al. [20] have reported Type IV loading dependence for water diffusion in CHA zeolite, that has windows of 0.38 nm size, in the presence of extra-framework Ca^{++} ions. Their explanation for Type IV behavior is somewhat different and such behavior is commonly observed in zeolites with 8-ring windows. The cations are the preferred adsorption sites for water molecules. When these sites are fully occupied, the additional water molecules can move more freely and this leads to a sharp increase in the self-diffusivity.

3. Conclusions

The explanation for the Type IV loading dependence of self-diffusivity of a variety of guest molecules in micro- and mesoporous materials, with pore sizes larger than 0.74 nm, can be traced to molecular clustering. An indication of molecular clustering is obtained when the inverse thermodynamic factor exceeds unity. We have presented arguments to suggest that Type IV behavior can be expected in nanoporous structures such as zeolites and MOFs with pore sizes larger than 0.74 nm when either (1) the operating temperature is below the critical temperature of the guest molecule or (2) when there is a strong degree of hydrogen bonding.

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Appendix A. Supplementary data

Supplementary material contains video animations, obtained from MD simulations, that demonstrate clustering. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2011.01.002.

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