Isotopic separation of H_2 and D_2 in SWCNTs: Thermodynamic and kinetic effects

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Introduction

The separation of gaseous substances from a mixture is one of the most relevant and energy consuming industrial processes nowadays. It is estimated that a 10-15% of the world total energy production is devoted to this operation[1]. A particular case is the separation of isotopologues, specially H_2 and D_2. This step is crucial for the nuclear energy and solvent chemistry industries, but due to the extremely similar physicochemical properties of the species it requires complex processes which increases the production costs. Nanostructured materials, such as zeolites, carbon-based materials and metal-organic frameworks, provide with an alternative to such processes due to the *quantum sieving* effect, which results in a difference on the adsorption and diffusion of isotopologues when confined in these materials[2,3]. In this work we aim at the study of the quantum sieving in narrow (8,0) single-walled carbon nanotubes from a thermodynamic and a kinetic point of view.

Kinetics: Diffusion Rate Calculation

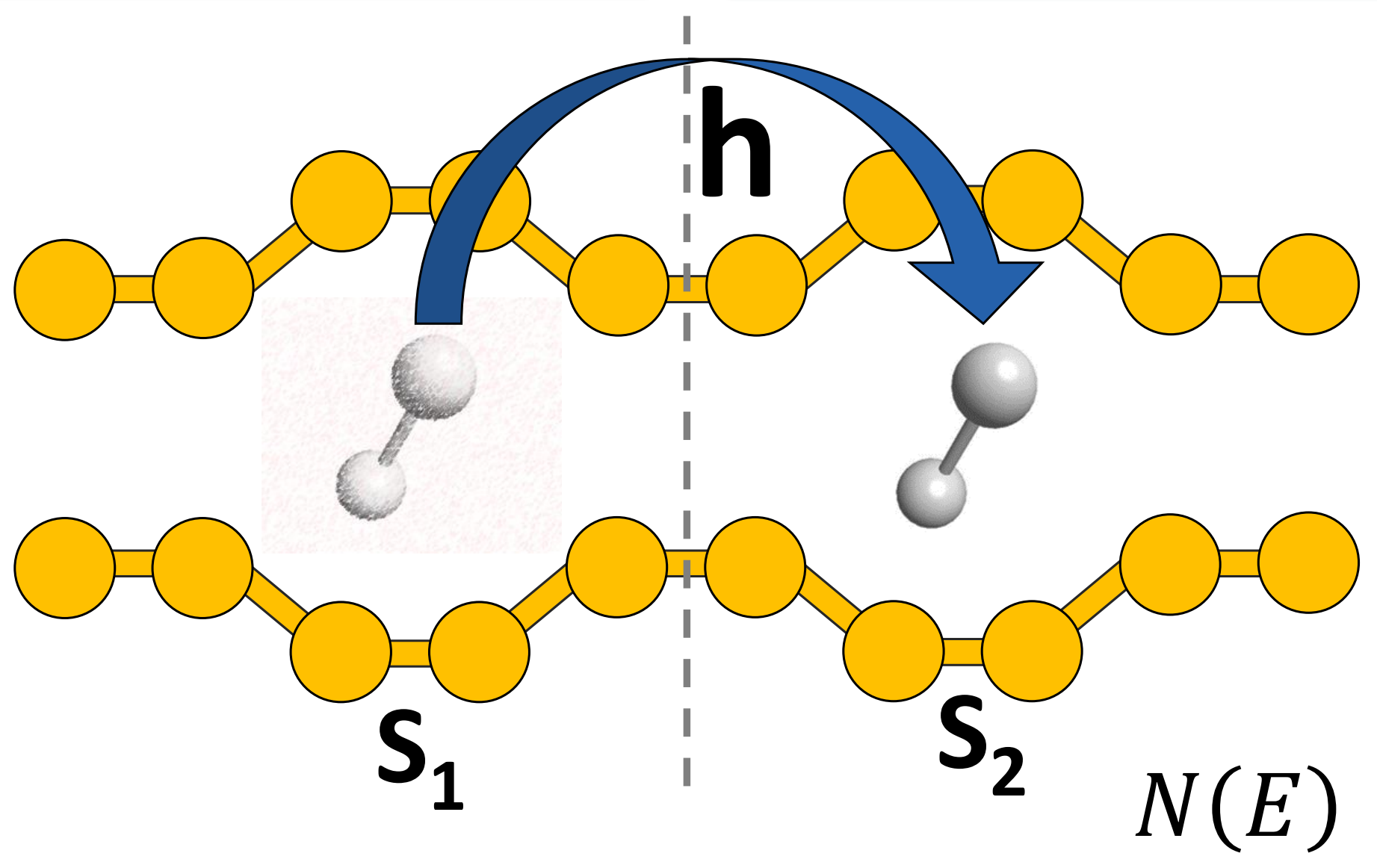
Single-hopping approach

In the low pressure limit, where we we can neglect intermolecular interactions, the diffusion of a particle in a material can be related with the probability of a single particle passing from an adsorption site S_1 to another contiguous, S_2[4]:

$$D(T) = \frac{l^2_{S_1 S_2}}{2d} k_{hop}(T)$$

k_{hop} is calculated as the rate of a molecule passing from site S_1 (reactants) to S_2 (products):

$$k_{hop}(T) = \frac{1}{2\pi \mathrm{hQ_r}} \int_{-\infty}^{\infty} N(E) e^{-E/RT} dE$$



N(E) Calculations

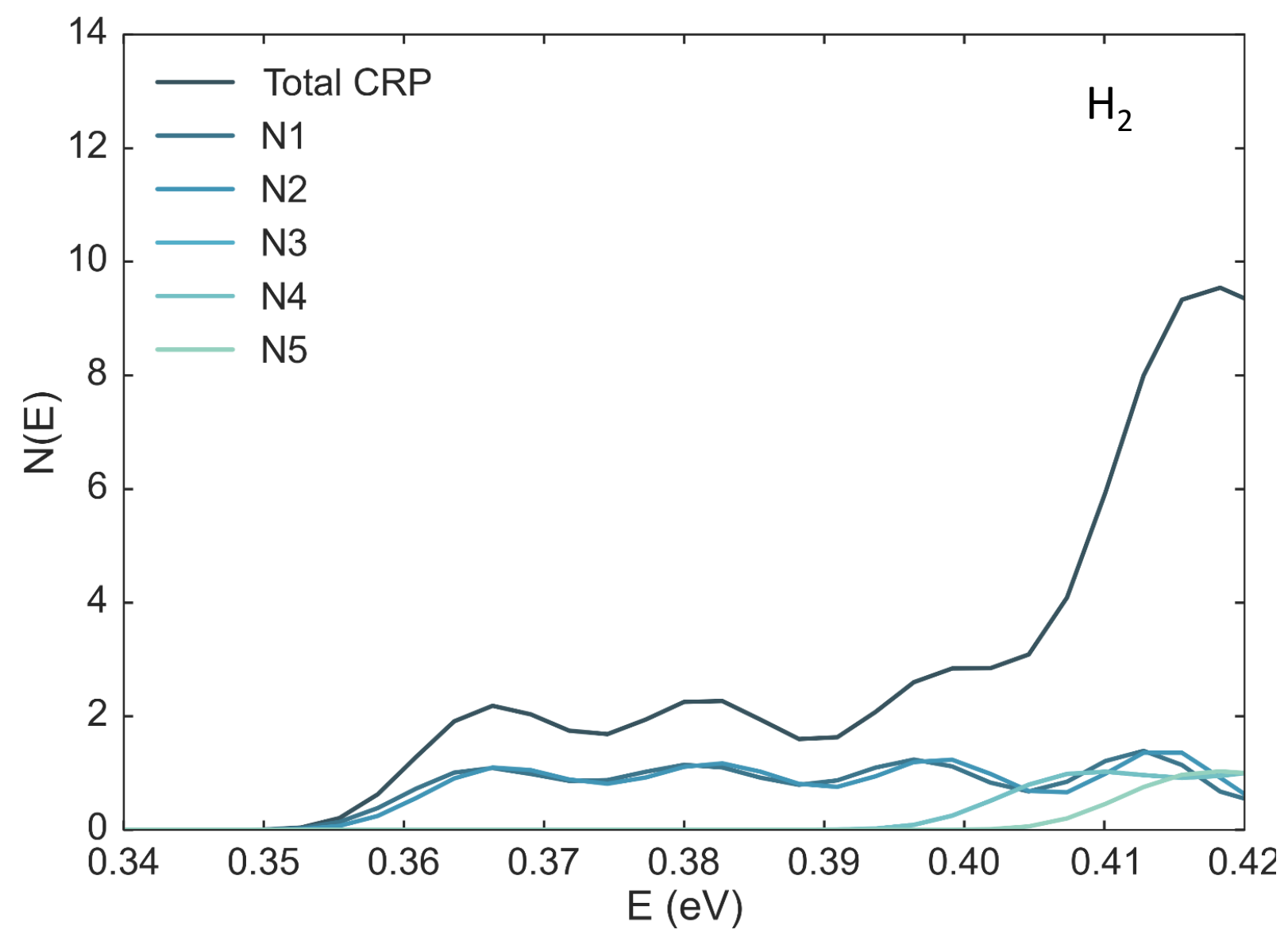
The *flux correlation function* approach[5] provides with an efficient way to calculate *N(E)*. It is based on the calculation and propagation of the eigenstates of the *flux operator*, $\hat{F}(\hat{H}, \hat{h})$, on any dividing surface h separating reactants from products:

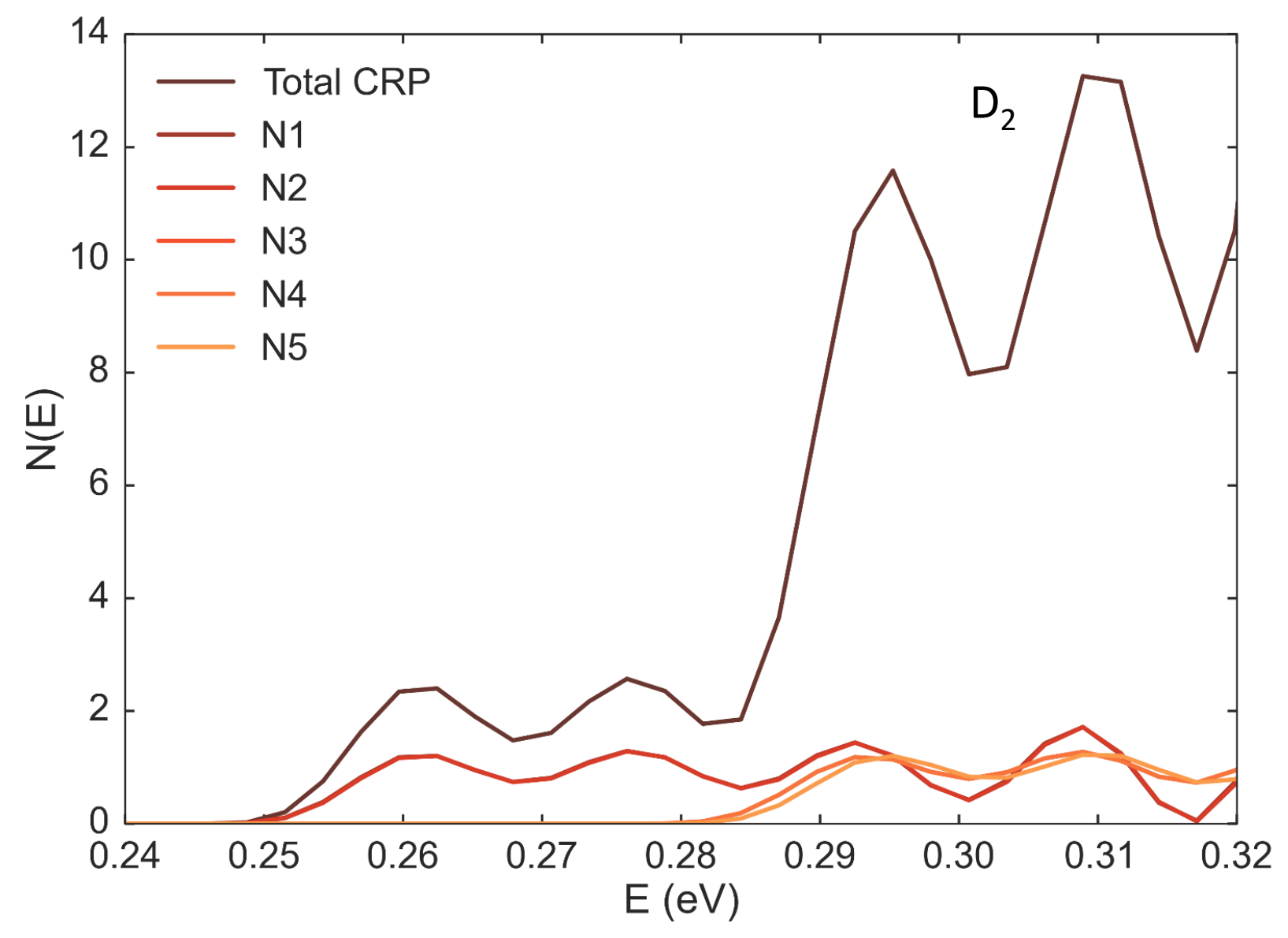
$$N(E) = \frac{1}{2} e^{\beta E} \sum_{f_{T_0}} \sum_{f'_{T_0}} f_{T_0} f'_{T_0} \left| \int_{-\infty}^{\infty} dt\, e^{iEt} \langle f_{T_0} \mid e^{i\hat{H}t} \mid f'_{T_0} \rangle \right|^2$$

The flux eigenstates are computed and propagated using the Multiconfigurational Time-dependent Hartree (MCTDH) approach[6].

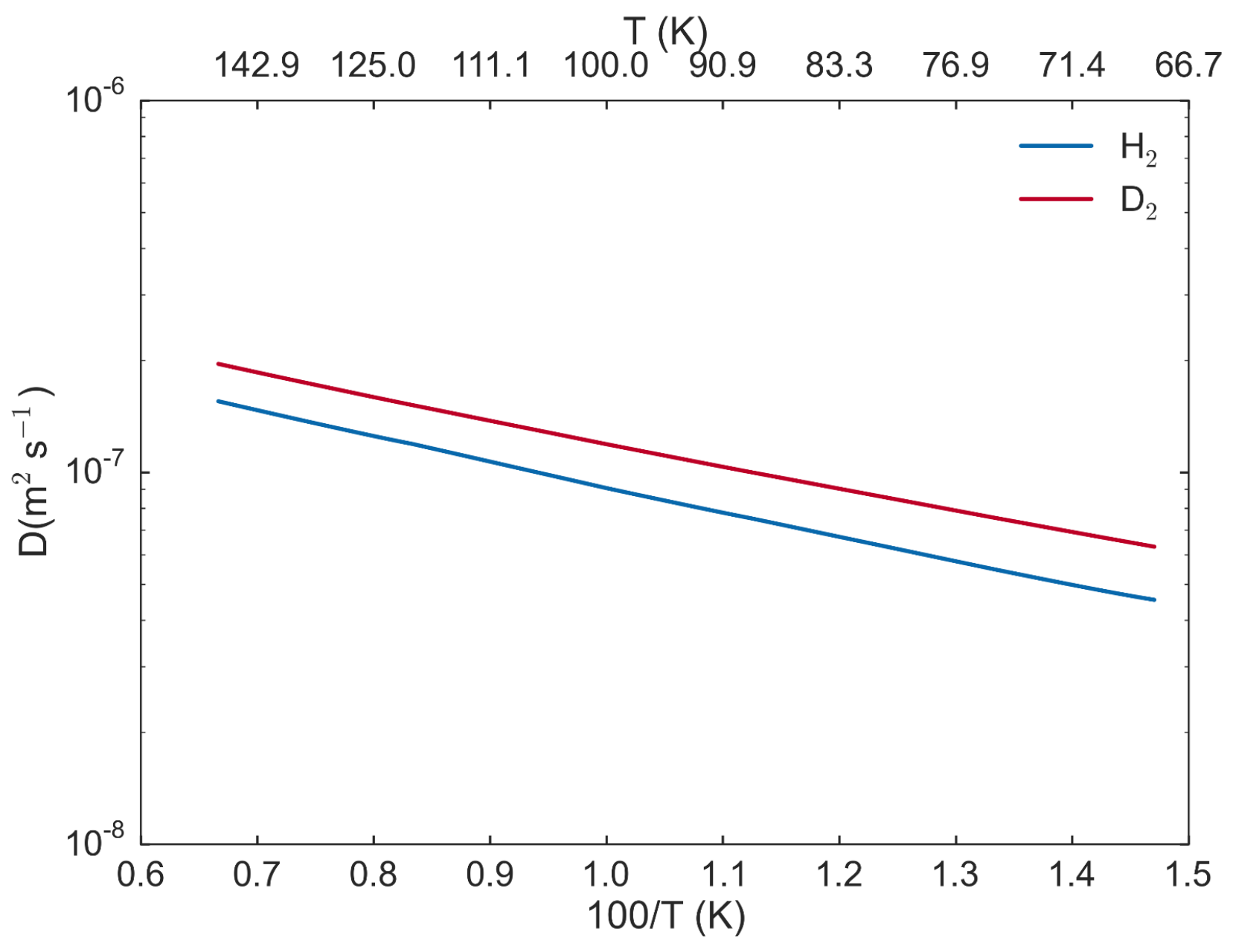
Results

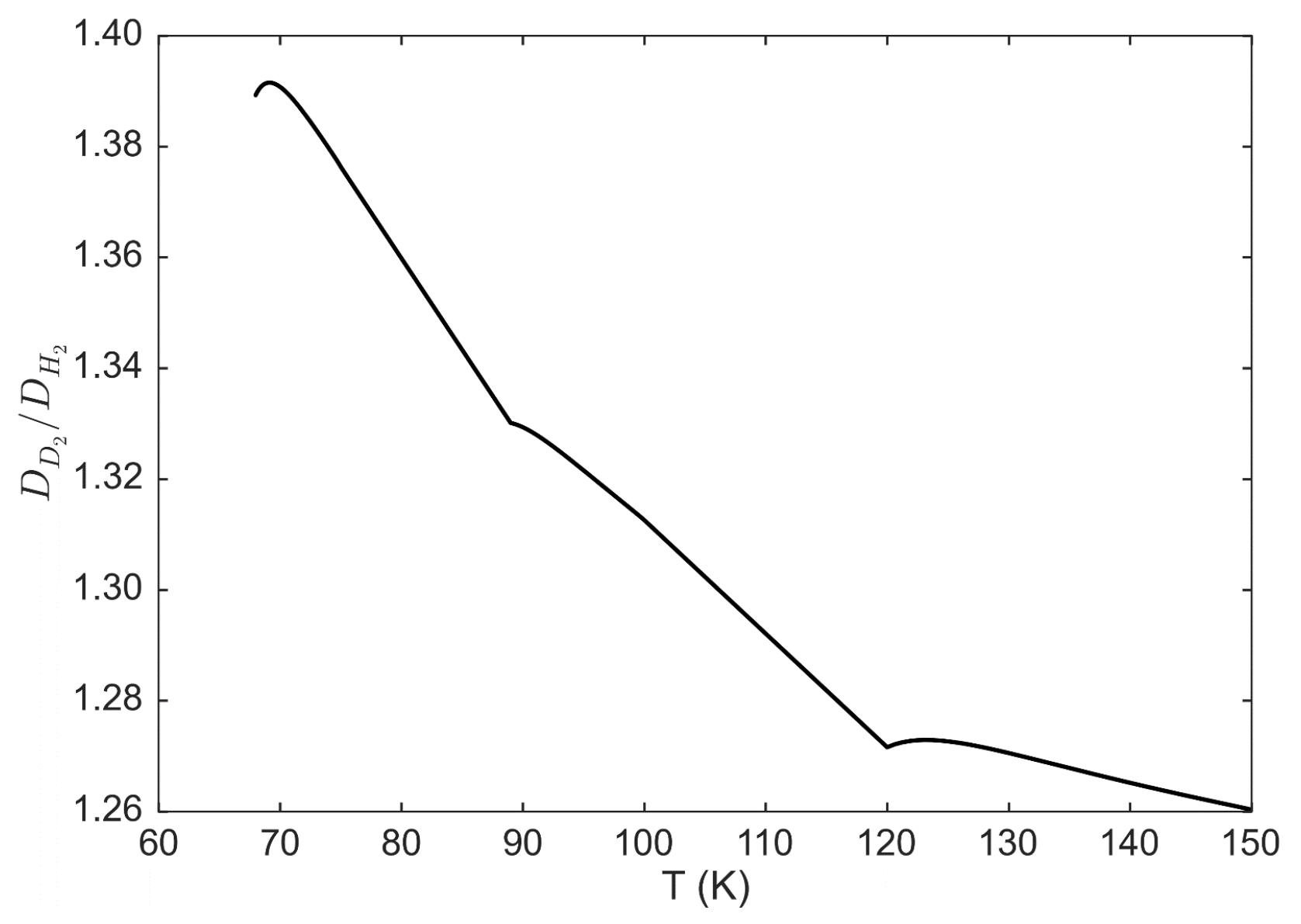
Comparison of reaction probabilities for H_2 and D_2 shows two important points: first, the energy threshold needed to start to populate reactive states is lower for D_2 than for H_2. Second, the density of these reactive states is larger for D_2 that for H_2.





The diffusion rate for D_2 is slightly larger for D_2 than for H_2, opposing the usual kinetic isotope effect but consistently with experimental studies on similar systems[7]. Differences increase at lower temperatures, as quantum effects become increasingly important.





Thermodynamics: Selectivity factor

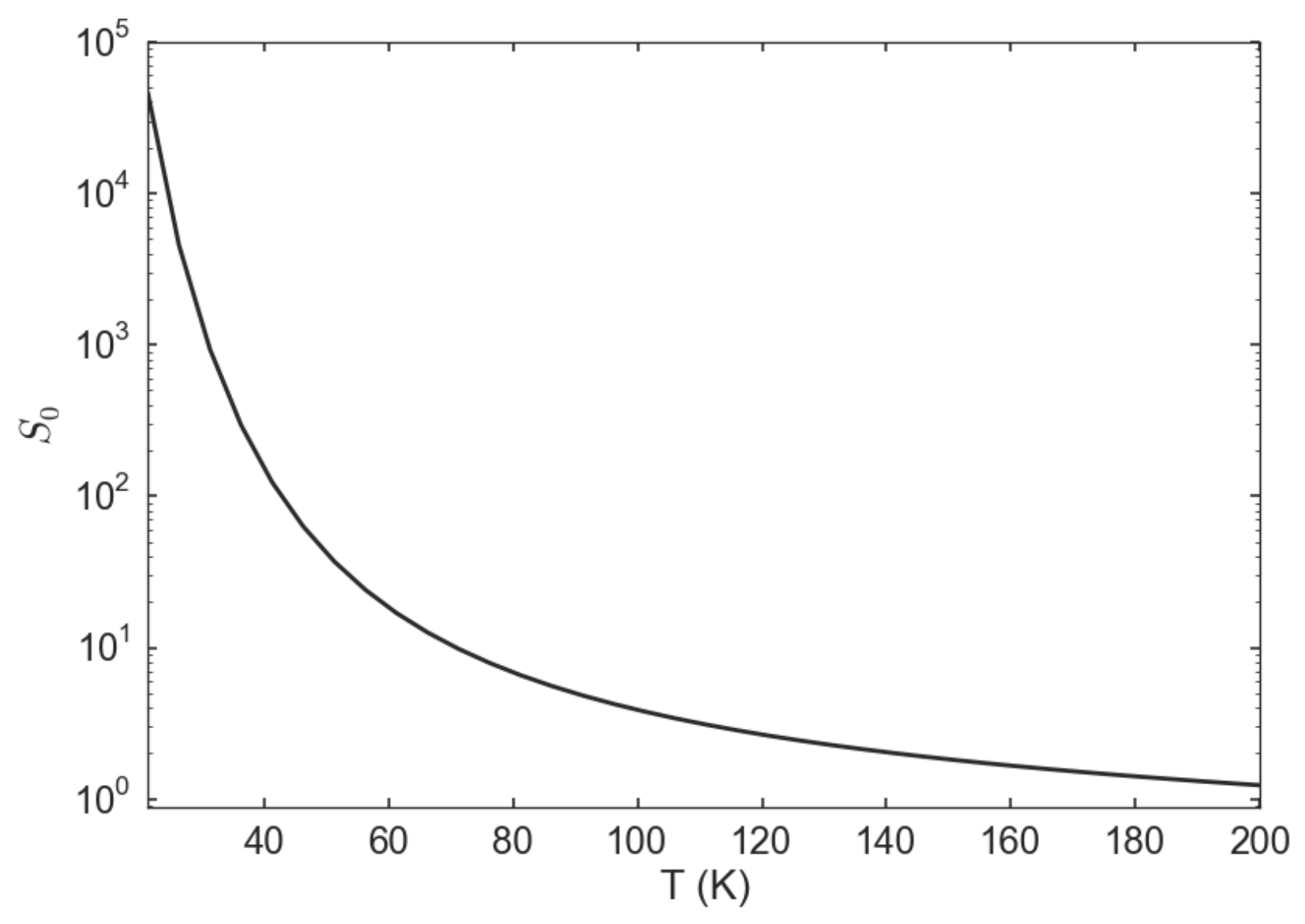
The thermodynamics of adsorption is directly related with the ratio of adsorption equilibrium constants of D_2 in front of H_2[6]:

$$S_0(D_2/H_2) = \frac{K^{ads}_{D_2}}{K^{ads}_{H_2}} = \frac{Q_{ads,D_2} Q_{free,H_2}}{Q_{ads,H_2}\ Q_{free,D_2}}$$

The free particle partition functions are calculated using the semiclassical approximation. For the adsorbed molecules, the quantum partition function is explicitly computed in order to take into account all confinement effects:

$$Q_{ads}(T) = g_e \sum_{n_{even}} e^{-\beta E_{n_{even}}} + g_o \sum_{n_{odd}} e^{-\beta E_{n_{odd}}}$$

Results



The selectivity factor S0 is extremely high at low temperatures, meaning that the adsorption of D_2 is greatly preferred in front of H_2. Even at moderate temperatures, a significant sieving is present. This is a result of the lower Zero Point Energy of D_2 with respect to H_2.

Conclusions

Hydrogen and deuterium have a distinct behaviour when confined in nanostructured materials with pores of the order of the nanometre. D_2 is preferentially adsorbed in a narrow carbon nanotube, with a selectivity factor grater than 100 at temperatures below 50 K, which points to the possible use of CNT bundles as separation devices. This is a result of the different zero point energy of H_2 and D_2, which largely increases the number of available states inside the nanotube for D_2, thus favouring its adsorption. Furthermore, once in the nanostructure, D_2 also diffuses faster than H_2, contrasting with the usual kinetic isotope effect, which usually implies a faster rate for the lighter isotopolgue. The explanation for this lies on the different amount of distortion due to quantum confinement effects for H_2 and D_2: the former, being lighter and being more strongly influenced by quantum confinement, suffers a greater distortion of the energetic levels which results in a larger effective radius, partially hindering the diffusion process.

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