

## Electronic supplementary information for PCCP

# Remarkable Nanoconfinement Effects on Chemical Equilibrium Manifested in Nucleotide Dimerization and H-D Exchange Reactions

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### On the role of entropy in the NCECE effect

The probability distribution of the reaction extent (proportional to the reaction mixture energy) becomes quite broad for small systems, as was shown in Fig. 6. On the other hand, the probability distribution in a macroscopic system is sharply peaked (similarly to Fig. 6a). Hence, the number of accessible microstates in the latter case practically coincides with the number,  $\Omega(E)$ , of microstates having the most probable energy,  $E$ , and the entropy reads,

$$20 \quad S = k \ln \Omega(E). \quad (\text{S1})$$

in accordance with Boltzmann's formula.

Furthermore, if long-range interactions are absent, interface effects between two parts (1) and (2) of the system, having most probable energies  $E_1$  and  $E_2$  ( $E = E_1 + E_2$ ), can be neglected.

25 Therefore, the two parts can be considered as non-interacting systems and the total number of system microstates equals the product,

$$\Omega(E) = \Omega(E_1)\Omega(E_2). \quad (\text{S2})$$

Combining eqs. (S1) and (S2) gives,

$$30 \quad S = S_1 + S_2, \quad (\text{S3})$$

namely, the known additivity (extensivity) of the entropy in a macroscopic system.

In case of small systems characterized by a broad probability distribution, the Boltzmann–Gibbs–Shannon entropy

$$35 \quad S = -k \sum_i p_i \ln p_i. \quad (\text{S4})$$

involving summation over all accessible microstates with different energies should be used instead of eq.(S1).

The violation of eqs.(S1-S2) for small systems makes the entropy intrinsically nonextensive. The nonextensivity can be quantified by introducing a parameter,

$$r^{nex} \equiv \frac{S_{2n} - 2S_n}{S_{2n}},$$

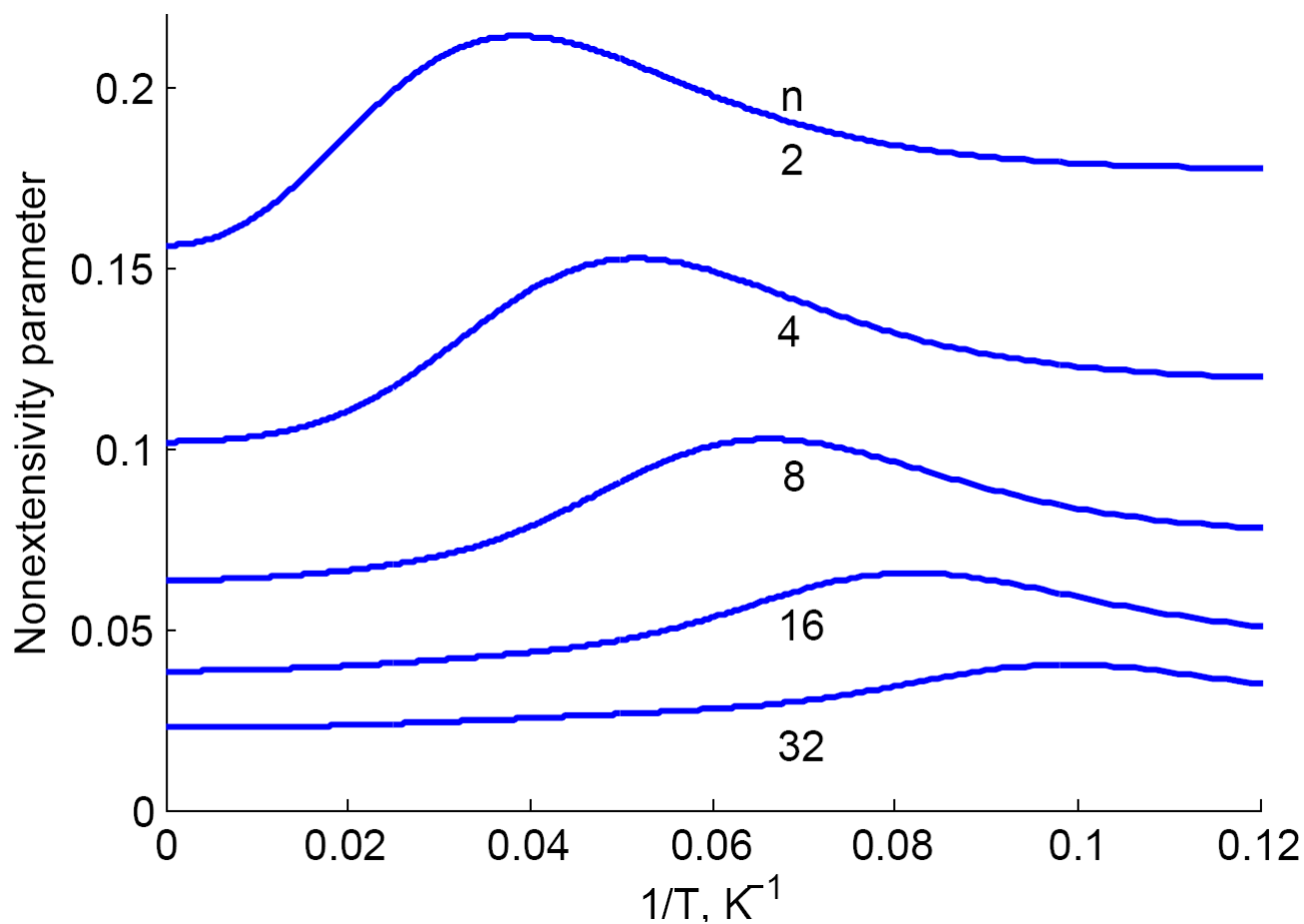
where  $S_n$  denotes the entropy of a reaction mixture comprising of  $n$  molecules. In case of the  $2HD=H_2+D_2$  reaction, the computed  $r^{nex}$  is positive, denoting "superadditivity" ("superextensivity") of the entropy. Furthermore, as demonstrated in Fig. S1, it exhibits gradual increase with decreased system size, while its maximum shifts to higher temperatures, matching approximately the slope changes in Fig. 5. Thus, the NCECE effect is related to the nonextensivity of the entropy of small systems.

Further elucidation of the NCECE origin is obtained via the reactant-product mixing entropy computed for this reaction. It

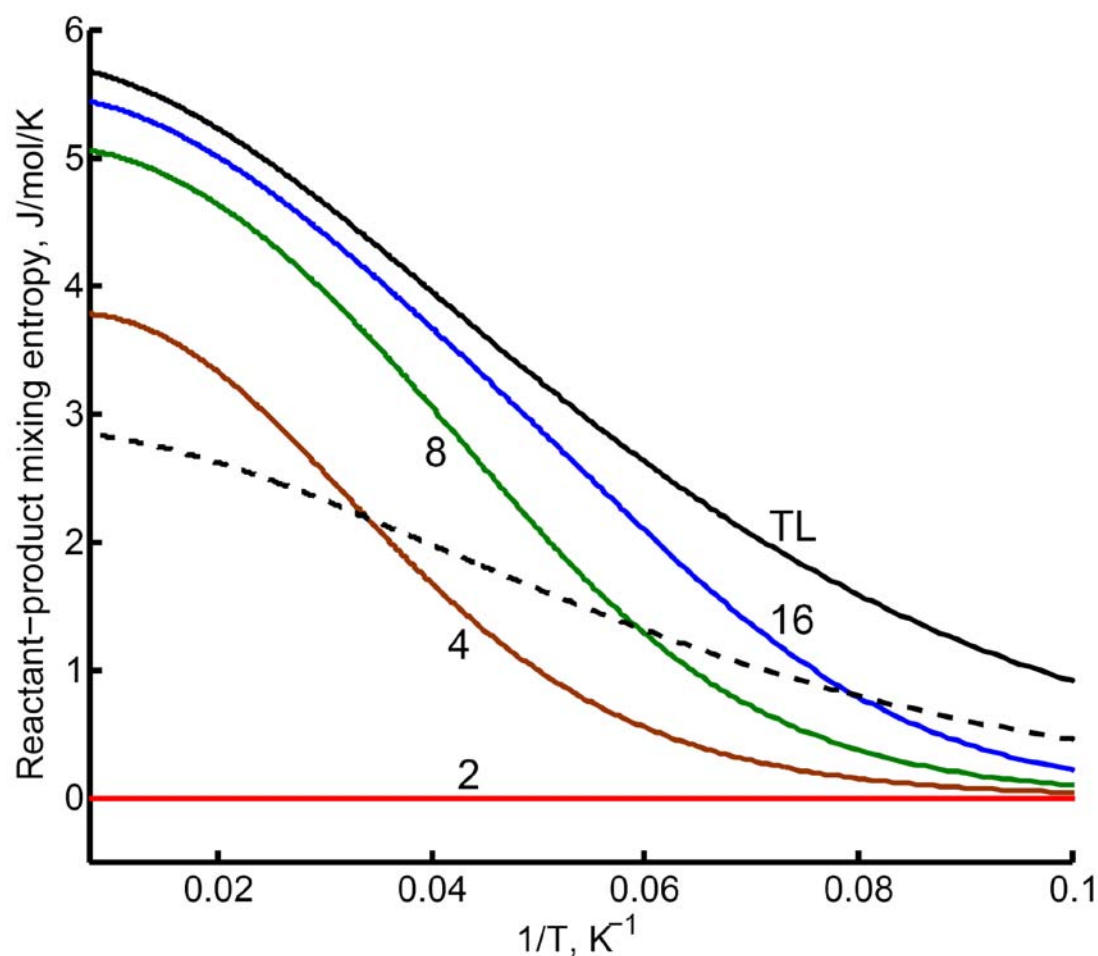
changes concurrently with the broadening and shape variations of the probability distribution function of the equilibrium reaction extent given in Fig.6. Thus, the mixing entropy (per mol) decreases with decreased numbers of molecules ( $n$ ) at all temperatures until it vanishes completely in case of  $n = 2$  (Fig. S2). Furthermore, due to a smaller number of "mixed" reactant-product microstates in smaller systems, the onset of the backward reaction and the corresponding increase in entropy (for  $n > 2$ ) occur at higher temperatures. It can be noted, the deviation from the TL curve and the concomitant approach to the  $n = 2$  zero line at low temperatures (Fig. S2) correspond to the slope doubling in Fig. 5. The inherent absence of the mixing entropy driving force for the backward reaction  $H_2+D_2 \rightarrow 2HD$  in the case of  $n = 2$  results in  $\xi \approx 1$  (Fig.6d), namely, the reaction is shifted almost completely towards the products, highlighting the dominant role of the nonextensive mixing entropy in the NCECE.

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**Fig. S1.** Variations of the nonextensivity computed for different total numbers of molecules in the  $2HD=H_2+D_2$  reaction mixture (the case of total coverage 0.5). With increasing  $n$ , the nonextensivity gradually decreases and its maximum shifts to lower temperatures that approximately match the slope changes in Fig. 5.



**Fig. S2.** Variations of the reaction mixing entropy computed for different total numbers of molecules  $s$  in the  $2HD=H_2+D_2$  stoichiometric reaction mixture (the case of total coverage 0.5). The dashed line (halfway between TL and the  $n = 2$  zero line) marks transitions between the corresponding mixing entropy values, which approximately match the slope changes in Fig. 5.

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