Semiempirical Model for Adsorption of Binary Mixtures

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SUPPORTING INFORMATION

Adsorption preference reversal: an entropic point of view

As it can clearly be observed in Figure 1a and 2a in the paper, the total coverage of the biggest species (in this case $k = 6$) has a maximum and later decreases to a limit value. This behavior is known as adsorption preference reversal (APR) and has also been observed in theoretical calculations and Monte Carlo simulations [1, 2]. The APR phenomenon usually is attributed to presence of repulsive mutual interactions.

The introduction of repulsive mutual interactions is a fictitious or effective way of taking into account geometric or steric effects between two species of different size. In this supplementary material we explain how this effect can be easily understood from an entropic point of view. Let us consider the adsorption of a binary mixture of hard rigid rods on one-dimensional lattices[3] at low pressures. In this case, the system behaves as single-component system and therefore, we can use the exact one-dimensional isotherm and the configurational entropy per site for k-mers [4],

$$\exp \beta(\mu - k\epsilon_k) = \frac{\theta \left[1 - \frac{(k-1)}{k}\theta\right]^{k-1}}{k(1-\theta)^k}, \tag{S1}$$

$$\frac{s(\theta)}{k_B} = \left[1 - \frac{(k-1)}{k}\theta\right] \ln\left[1 - \frac{(k-1)}{k}\theta\right] - \frac{\theta}{k}\ln\frac{\theta}{k} - (1-\theta)\ln(1-\theta), \tag{S2}$$

where k_B denote the Boltzmann constant.

In order to understand why the biggest molecules are adsorbed at low pressures, let us consider the adsorption isotherm eq S1 for different k-mers sizes. As it can be seen in Supp Fig 1, the largest species are adsorbed more quickly than the smaller ones. From an entropy point of view this means that the number

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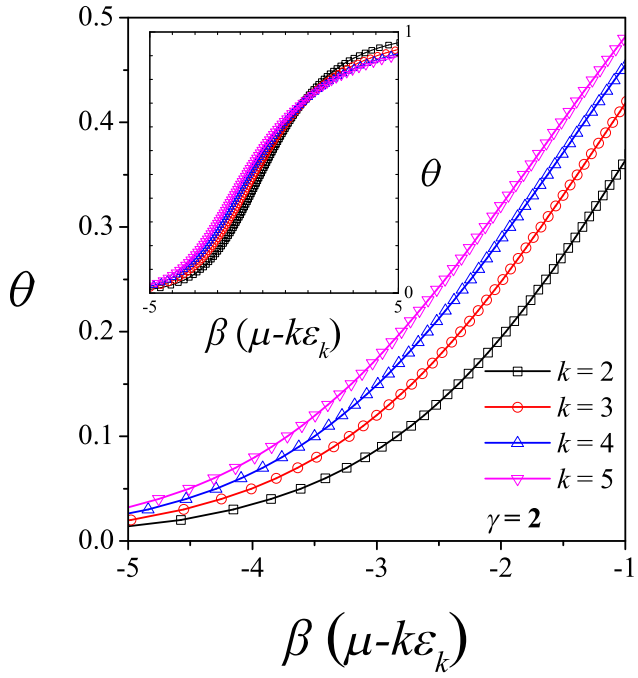
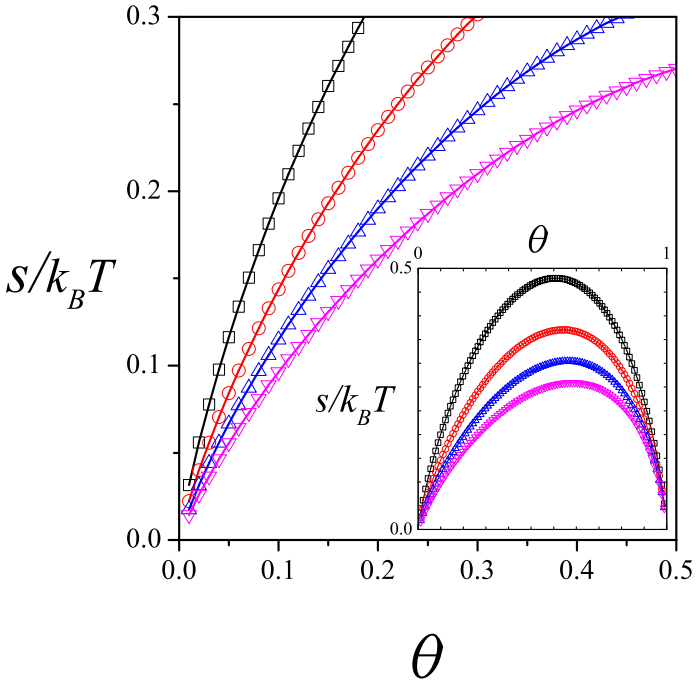


Supplementary Figure 1: Adsorption isotherm for a single-gas of noninteracting k-mers on one-dimensional lattices. The different symbols and colors represent different sizes of k (see eq S1).

of available states to adsorb the largest molecules are occupied faster than the smaller ones (see Supp Fig 2).

The APR phenomenon is also observed in our Monte Carlo simulations. We included a movie showing this effect for a binary mixture of dimers ($k = 2$) and trimers ($l = 3$), with molar fraction $y_k = 0.7$ and $y_l = 0.3$, respectively, on a square lattice ($\gamma = 4$).



Supplementary Figure 2: Configurational entropy per site vs. surface coverage for the cases reported in Supp Fig 1.

References

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