

## Enhancing the separation of enantiomers in adsorbed overlayers: a Monte Carlo study

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The influence of external factors on the chiral resolution of enantiomers in adsorbed overlayers has been especially interesting from the perspective of creation of chiral surfaces. Chiral segregation of this type can be induced or enhanced, for example, by an external unidirectional fields such as magnetic or electric field. To explore the effect of an external field on the 2D chiral resolution of model enantiomers we performed canonical Monte Carlo simulations on a square lattice of equivalent adsorption sites. The adsorbed molecules which are sensitive to the external field, were assumed to consist of four identical segments and they were able to adopt four possible orientations on a square lattice. Short-range segment-segment interactions limited to the nearest neighbours on the lattice were allowed to account for the intermolecular interactions. The calculations were performed for two exemplary molecular structures and the strength of the external field was gradually increased in each case. The preliminary results described herein demonstrate that continuously changed external fields can induce chiral resolution of enantiomers of appropriate geometry. The insights from this study can be useful in developing strategies for 2D chiral separations in which external stimuli are used.

**Keywords:** adsorbed overlayers, chiral resolution, self-assembly, external field

## 1. INTRODUCTION

Formation of chiral adsorbed overlayers can occur due to adsorption of both chiral and prochiral molecules on solid substrates, leading to the creation of mirror image domains [1]. The spontaneous segregation of enantiomers into homochiral domains has been observed in a number of cases [2-4], but this process is difficult to control and it usually depends on many external parameters (e.g. temperature, concentration etc.). One factor which has been found to enhance the chiral segregation is the unidirectional positioning of the adsorbed molecules which can be imposed by the underlying surface or by external fields. For example, this effect has been observed for the surface-assisted resolution of prochiral derivative of quinacridone adsorbed on Cu (110) whose atomic rows are guiding lines for the adsorbed enantiomers [10]. Similarly, using unidirectional magnetic field in combination with liquid crystal imprinting uniaxial arrangement of prochiral molecules adsorbed on graphite surface has been obtained [11]. In order to understand and predict the chiral separation in adsorbed overlayers, one can use theoretical methods such as the Monte Carlo (MC) simulation method. MC simulations have been performed for a variety of simplified molecular chiral structures adsorbed on energetically homogeneous surfaces, including bent needles [5], tripods [6] and other polyatomic molecules [7, 8]. These studies have demonstrated that the main effect on the chiral separation exert: density of the adsorbate [9], geometry of the molecules and intermolecular interactions. Careful manipulating of these factors makes it possible to start-up or enhance the self-organization of adsorbed species. In this contribution we use the MC simulation method to assess the effect of uniaxial external field with continuously changing strength on the 2D segregation of surface enantiomers of a prochiral molecule. To that end we use a modified version of the model proposed previously [10] and we additionally compare the simulated results with those obtained for a molecule with the same composition but different geometry.

## 2. MODEL AND SIMULATION

We consider four-segment molecules **A** and **B** (Fig. 1) adsorbed on a planar surface represented by a square lattice of equivalent adsorption sites. Note that, molecule **A** is chiral in 2D yet because of the  $\Gamma$ -shaped geometry. In the case of molecule **B**, the source of chirality is the dipole

moment without which this molecule is achiral in 2D. Each enantiomer of the prochiral molecule **A** was allowed to adopt one of the four possible orientations on the lattice. The same orientations were assumed for the molecule **B** shown in the right panel. The molecules were allowed to interact via short-range segment-segment interaction potential limited to the nearest neighbours on a square lattice, as shown in the bottom part of Fig. 1.

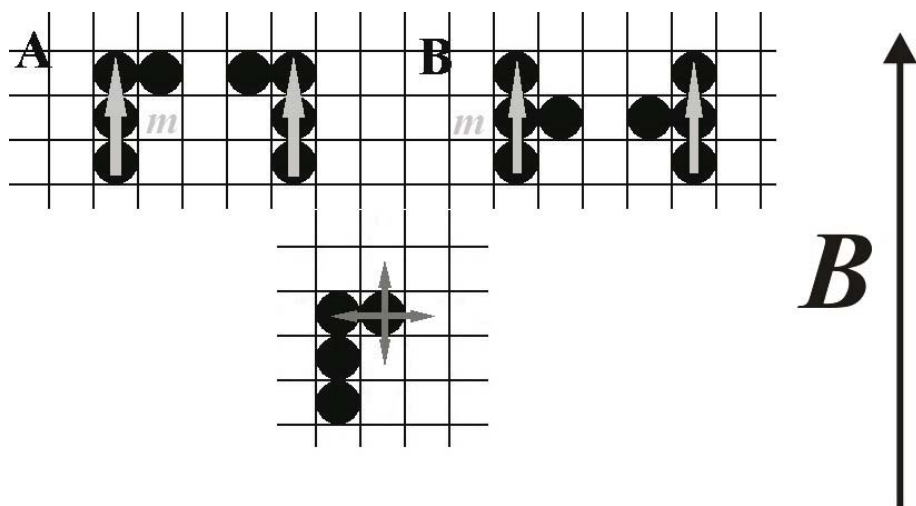


Fig. 1. The molecules **A** and **B** used in the simulations. Molecular (magnetic or electric) moment  $m$  aligned parallel to the long molecular arm of **A** and **B** and the direction of the external field  $B$  are shown by the grey and black arrows, respectively. The arrows in the bottom part show the range of segment-segment interaction assumed in the model.

The energy of interaction between a pair of neighbouring segments was characterised by the parameter  $\varepsilon = -2$  expressed in  $kT$  units. To take into account sensitivity of the molecule to the external field we assumed that it has a (magnetic or electric) dipole moment parallel to the long molecular axis. Energy of the adsorbed molecule in static field parallel to the surface is given by the scalar product of vectors  $m$  and  $B$ :

$$E = -\mathbf{m} \cdot \mathbf{B} = -mB \cdot \cos\theta \quad (1)$$

where  $m$  is the dipole moment of the molecule (in our studies  $m = 1$ ),  $B$  is the strength of the field and  $\theta$  is the angle between  $m$  and  $B$ . Although, there are four possible orientations of the molecules, there are only three possible values of the energy  $E$ , that is:  $-mB$  for  $m$  facing upwards (Fig. 1),  $mB$  for  $m$  facing downwards and zero for  $m$  aligned horizontally.

The simulations were performed on a 100 by 100 lattice with 900 adsorbed molecules (racemic mixtures) using the conventional canonical ensemble with Monte Carlo method for rigid polyatomic molecules with orientationally biased sampling [11]. Periodic boundary conditions were imposed to eliminate edge effects. The simulation algorithm was organized as follows. At the beginning of the simulation the molecules were randomly distributed over the surface. Next a molecule was chosen randomly and trial displacement was attempted by random choice of new coordinates of the reference segment of that molecule. In a new place four trial orientations were generated by rotating the molecule around the reference segment and for each of these trial orientations potential energy was calculated (sum of segment-segment interactions and coupling with external field). The same calculations were performed in the original position of the molecule. To determine the acceptance probability of the new configuration we defined the Rosenbluth factor for both old ( $W_o$ ) and new ( $W_n$ ) position:

$$W_o = \exp[-\beta U_0] + \sum_{i=1}^3 \exp[-\beta U_i] \quad (2)$$

$$W_n = \sum_{i=1}^4 \exp[-\beta U_i] \quad (3)$$

$U_0$  – potential energy in initial orientation,  $U_i$  – potential energy in trial orientation  $i$ ,  $\beta = (kT)^{-1}$  where  $k$  is the Boltzmann constant

Next, one of the orientations in the new position was selected with the probability:

$$p_j = \frac{\exp[-\beta U_j]}{\sum_{i=1}^4 \exp[-\beta U_i]} \quad (4)$$

Comparison of the ratio of the Rosenbluth factors in the new and the old position with a random number  $r \in (0,1)$  allowed us to decide whether the move should be accepted or rejected. Specifically, if  $W_n/W_o$  was greater than  $r$ , the new position and orientation of the molecule was accepted. Otherwise the molecule was left in its original position. The simulations were performed using up to  $10^8$  MC steps, where one MC step is a single trial to move (and rotate) each of  $N$  molecules to a new position on the lattice.

### 3. RESULTS AND DISCUSSION

Figure 2 shows snapshots of the overlayers obtained for molecules **A** and **B** (racemates) without the external field. For clarity the enantiomers of **A** and **B** were coloured differently. As it can be seen in Fig. 2 both simulated overlayers are compact and strongly disordered with equal occurrence of the four orientations allowed in the model.

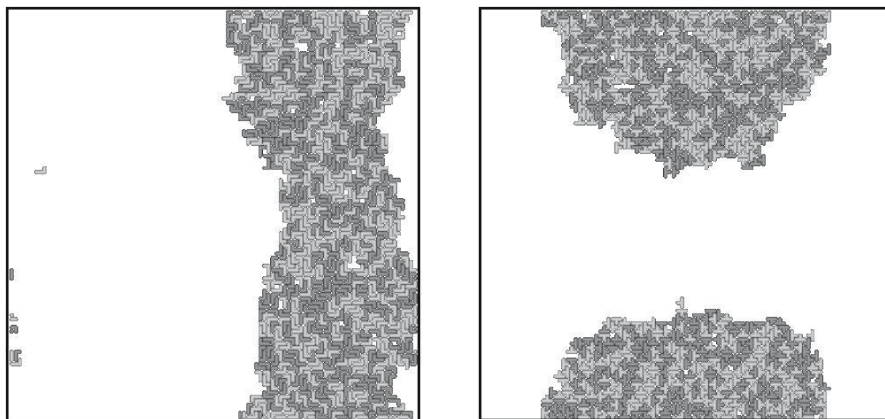


Fig. 2. Snapshots of the overlayers comprising 900 molecules of **A** and **B** (right) simulated under no external field.

When the strength of the external field increases, that is the product  $mB$  becomes larger, ordering of the adsorbed molecules occurs, so that the molecules are aligned parallel to the field, as shown in Fig. 3.

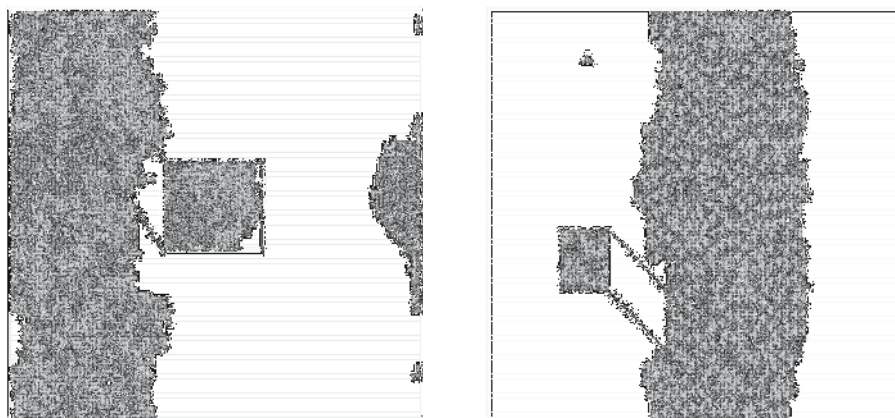


Fig. 3. Snapshots of the overlayers obtained for  $mB = 0.76$  (left **A**, right **B**). The insets in both parts are magnified fragments of the corresponding structures.

This tendency is more visible for **B** whose almost all molecules are oriented vertically. For the molecule **A** the external field is responsible for the growth of homochiral domains which are, however, still embedded in a pool of randomly oriented enantiomers.

Further increase of  $mB$  induces a complete separation of the enantiomers of **A** resulting in the creation of two large homochiral domains, as showed in Fig. 4. In the case of **B** the effect of the external field is only minor compared to the previous situation and it refers to the enhanced formation of alternate rows of molecules whose side segments face the opposite directions (see the inset, Fig. 4).

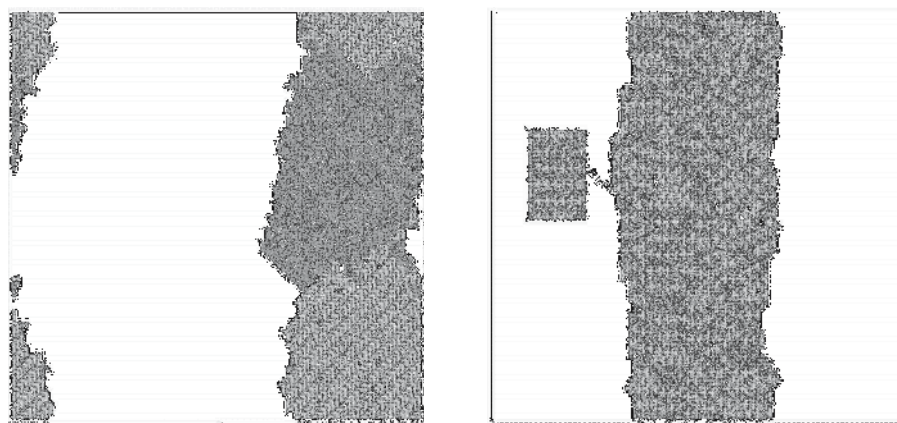


Fig. 4. Snapshots of the overlayers obtained for molecule **A** (left) and molecule **B** (right) for  $mB = 0.82$ . For molecule **A** two large homochiral domains can be observed. The inset in the right panel shows alternating rows in the domain of **B**.

To quantify the effect of the external field on the structure formation in the systems comprising molecules of **A** and **B** we calculated the average number of heterogenous segment-segment bonds in the simulated overlayers. This quantity means the average number of interactions that a single segment in the enantiomer of given type (colour) forms with foreign neighbouring segment.

As shown in Fig. 5, for the molecule **A** the number of heterogeneous bonds exhibits a rapid decrease at  $mB$  equal to about 0.8. This effect is a clear manifestation of the chiral resolution which minimizes the number of contacts between different enantiomers of **A**. In consequence above this critical value of  $mB$  the only contribution to the number of heterogeneous bonds comes from the molecules which are placed at the boundary of the contacting domains. For the molecule **B** we can observe

a different trend, that is the number of heterogeneous bonds increases with the strength of the applied field. In this case, the field is responsible for the formation of locally ordered structures of alternating rows of molecules of different colour. This structure offers more heterogeneous contacts compared to the structure obtained without the field for which numerous clusters comprising randomly oriented molecules of one colour can be identified (see Fig. 2).

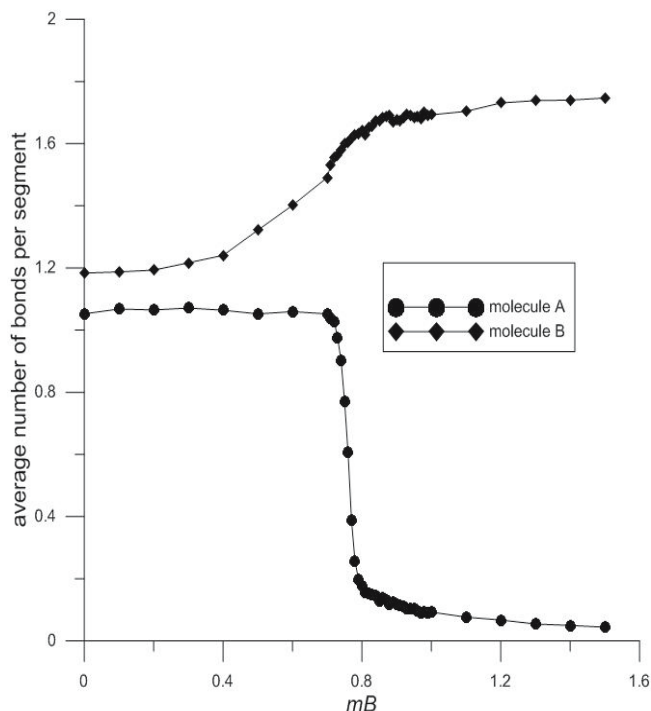


Fig. 5. Changes in the average number of heterogeneous bonds per segment as a function of the external field.

#### 4. CONCLUSIONS

The preliminary results of this work demonstrate that the directional external field can greatly promote separation of prochiral molecules into extended enantiopure domains. As we demonstrated, the segregation can be triggered by a substantial adjustment of a continuously changed uniaxial field. The conclusions from this theoretical studies can be useful in developing new experimental techniques in which directional magnetic or electric fields are used to induce controlled resolution of enantiomers



in adsorbed overlayers. To explore the dependency of the resolution on such factors as molecular geometry and density of the adsorbed phase further studies are needed and these factors are the subject of our ongoing research.

## REFERENCES

- [1] S. M. Barlow, R. Raval, *Surf. Sci. Rep.*, **50**, 201 (2003).
- [2] J. V. Barth, *Annu. Rev. Phys. Chem.*, **58**, 375 (2007).
- [3] J. Barth, G. Costantini, K. Kern, *Nature*, **437**, 671 (2005).
- [4] A. Kühnle, *Curr. Opin. Coll. Int. Sci.*, **14**, 157 (2009).
- [5] R. Perusquía, J. Peón, J. Quintana, *Physica A*, **345**, 130 (2005).
- [6] I. Medved', A. Trník, D. A. Huckaby, *Phys. Rev. E.*, **80**, 011601 (2009).
- [7] I. Medved', A. Trník, D. A. Huckaby, *J. Stat. Mech.*, **12**, P12027 (2010).
- [8] I. Paci, I. Szleifer, M. A. Ratner, *J. Am. Chem. Soc.*, **129**, 3545 (2007).
- [9] I. Paci, *J. Phys. Chem. C*, **114**, 19425 (2010).
- [10] P. Szabelski, A. Woszczyk, *Langmuir*, **28**, 11095 (2012).
- [11] D. Frenkel, B. Smit, *Understanding Molecular Simulation From Algorithms to Applications*, Academic Press, 2002.
- [12] H. Cun, Ye Wang, B. Yang, L. Zhang, S. Du, Yu Wang, K.-H. Ernst, H.-J. Gao, *Langmuir*, **26**, 3402 (2010).
- [13] A. M. Berg, D. L. Patrick, *Angew. Chem. Int. Ed.*, **44**, 1821 (2005).

## CURRICULA VITAE



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