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Explanation for the Emergence of a Single Chiral Solid State during Attrition-Enhanced Ostwald Ripening

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Supporting Information

Explanation for the emergence of a single chiral solid state during

attrition enhanced Ostwald ripening

-survival of the fittest-

Computational method: Derivation of the probability equation for Ostwald ripening

events

The Gibbs free energy of a crystal of n molecules is:

$$G(n) = -n\Delta\mu + \gamma(n),$$
(SI 1)

where $\Delta\mu$ is the difference in chemical potential for a molecule in the bulk solution and in

the bulk crystal, i.e. $\Delta\mu = \mu_f - \mu_s$. The surface free energy $\gamma(n)$ depends on the shape of

the crystal. To keep the model simple we assume that all crystals are perfect spheres, for

which the surface area can be expressed in terms of the number of molecules as:

$$A(n) = 4\pi\left(\frac{3n\Omega}{4\pi}\right)^{2/3},$$
(SI 2)

with Ω the molecular volume. The surface free energy can then be written as:

$$\gamma(n) = A(n) \cdot \gamma,$$
(SI 3)

where γ is the specific surface free energy. The driving force per molecule for an Ostwald

event for which a molecule is transformed from a crystal with n_i molecules to a crystal

with n_j molecules thus becomes:

$$\Delta\Delta\mu = \Delta\mu_{n_i} - \Delta\mu_{n_j} = \left(\frac{\partial G(n)}{\partial n}\right)_{P,T,n=n_i} - \left(\frac{\partial G(n)}{\partial n}\right)_{P,T,n=n_j}$$

$$= \frac{\gamma 8\pi}{3}\left(\frac{3\Omega}{4\pi}\right)^{2/3}\left[\left(\frac{1}{n_i}\right)^{1/3} - \left(\frac{1}{n_j}\right)^{1/3}\right] \tag{SI 4}$$

Assuming linear growth and dissolution kinetics, the probability $P_{Ost}(n_i, n_j)$ for such an Ostwald event is proportional to $\Delta\Delta\mu$, and can be written as:

$$P_{Ost}(n_i, n_j) = P_{Ost} \cdot \left[\left(\frac{1}{n_i}\right)^{1/3} - \left(\frac{1}{n_j}\right)^{1/3}\right]. \tag{SI 5}$$

The surface free energy γ and molecular volume, are therefore covered by the attrition parameter ξ defined in equation (1).

Initial racemic conglomerate: results for $\chi = 1$

Simulations with $\chi = 1$ starting with an initial racemic conglomerate, were performed as described for the case of $\chi = 0.1$. All the experiments end in a randomly distributed single chiral end state (figure SI 1). In contrast to the slowly racemizing conglomerates, stochastic behavior is observed in the case of instantaneous racemization in the solution. Also note that the total crystal surface area remains constant during the complete simulation, as shown in figure SI 2. In contrast to the case of $\chi = 0.1$, the deracemization time increases almost linearly with the size of the system N for all investigated attrition intensities, as can be observed in figure SI 3. This is caused by the intrinsically stochastic behavior of the process.

Initial enantiomeric excess: results for $\chi = 1$

Simulations were performed as described for $\chi = 0.1$. Figure SI 4 shows that for instantaneous racemization in the solution ($\chi = 1$) no amplification is observed. That is, the chance to end in an enantiopure D or L state equals the initial asymmetry.
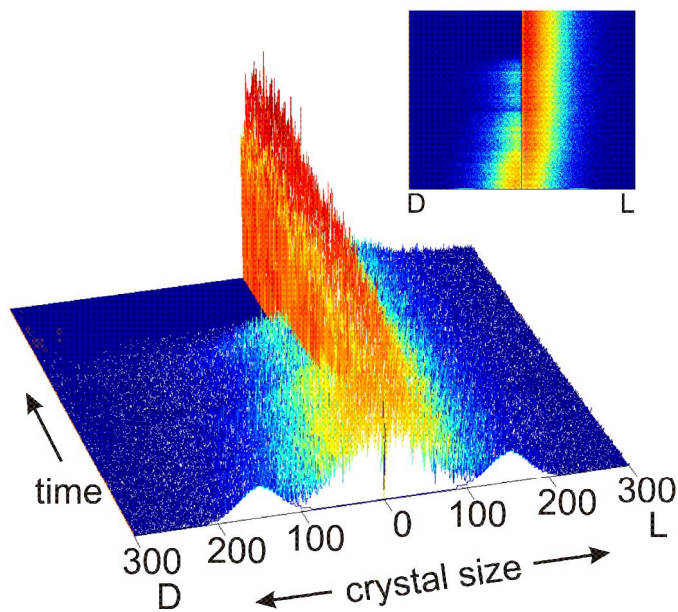
Figure SI 1. A typical example of the crystal size distribution (CSD) of D and L crystals during a Monte Carlo run simulating the combined process of attrition and Ostwald ripening for a compound achiral in solution ($\chi = 1$). The initial CSD is set to a racemic mixture of two Gaussian distributions each containing 10^5 molecules centered around a crystal size of 150 molecules. The attrition-ripening ratio is set to $\xi = 0.01$; $n_{min} = 10$. The graph shows the evolution of the CSD during 10^8 Monte Carlo events. The inset shows the top view of the graph. Note the large stochastic perturbations halfway the deracemization process.
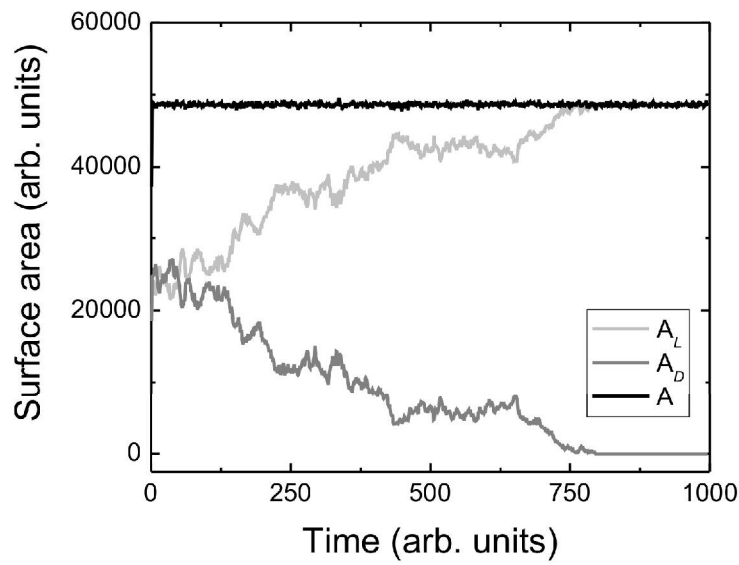
Figure SI 2. The total crystal surface area during the deracemization process. The graph shows the surface area during the simulation shown in figure SI 1 with A_D and A_L the total crystal surface areas of the D and L crystals respectively and A the sum of these two.
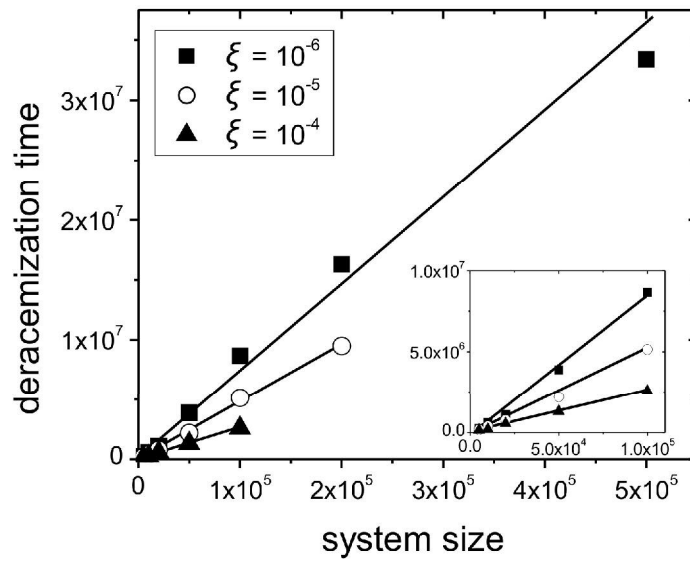
Figure SI 3. Deracemization time, t_{derac}, versus the system size N for different stirring rates with $\chi = 1$. The deracemization time increases almost linearly with the system size. For high values of the attrition-ripening

ratio ξ only limited values of N could be modeled within a reasonable simulation time. The insert shows a detail of the graph for small system sizes.
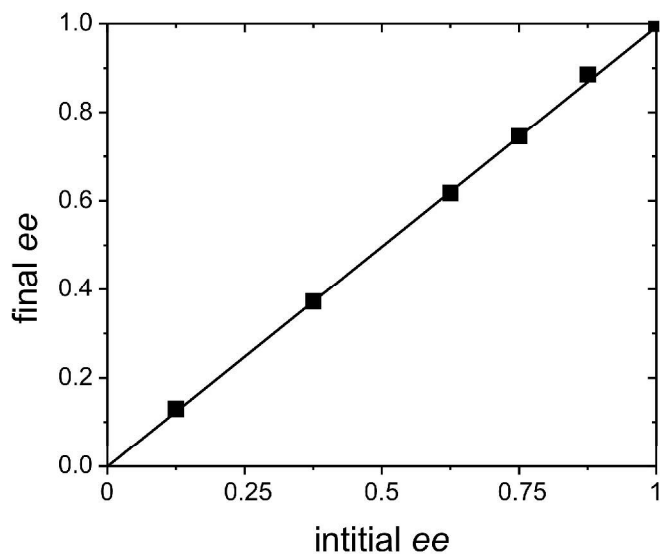
Figure SI 4. Final *ee* averaged over 1000 deracemizations as a function of the intitial *ee*, for a compound intrinsically achiral in solution ($\chi = 1$). Deracemizations were performed with an initial abundance of one enantiomer over the other but with both CSDs centered on the same mean value. Every point in the graph represents the mean final *ee* averaged over 1000 experiments. $\xi = 0.04$; $N = 8000$. The line is a guide to the eye.