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A Model for Complete Chiral Crystallization

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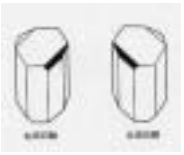
Background picture by H. Hibino

Enantiomorph of crystals

- Louis Pasteur discovered enantiomorph of tartaic acid (2,3-dihydroxy butanedioic acid)
  HOOC-CH(OH)-CH(OH)-COOH



Crystals of chiral molecules

Enantiomorph of crystals

- SiO_2(quartz)
  Low temperature quarts : $P3_121$ and $P3_221$

3 inches synthetic quartz crystal for wafer (Fine Crystal Co.)

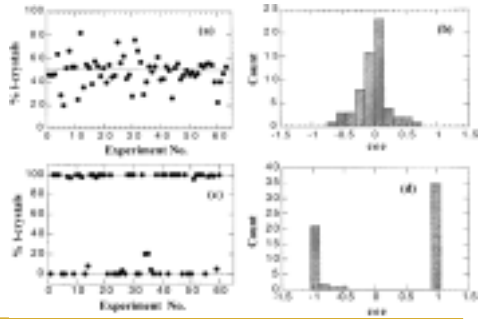
A chiral crystal made from the solution of achiral molecules

Chiral crystallization of $NaClO_3$

- Enantiomeric excess of spontaneously nucleated crystals

Without stirring

With stirring



D. K. Kondepudi, R. Kaufman and N. Singh: Science **250** (1990) 975.

Chiral crystallization of $NaClO_3$

- The strong symmetry breaking may be due to secondary nucleation

  Secondary nuclei can be generated from a suspended seed crystal due to solid contact and/or fluid convection.

  Secondary nucleation occurs at supersaturation levels at which the primary nucleation rate is negligible.

  At low supersaturation the secondary nucleation is highly enantioselective but at higher supersaturation it is less so.

R.-Y. Qian and G. D. Botsaris, Chem. Eng. Sci. **53** (**1998**) 1745.

Recent experiment: a route to complete chirality of $NaClO_3$

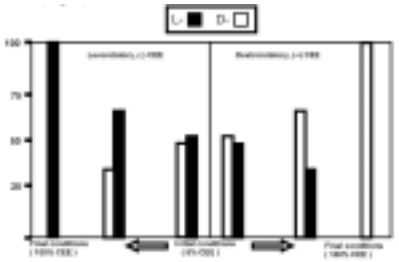
- Levorotatory and dextrorotatory crystals can be easily distinguished by a polarizer.

L crystals: blue, D crystals: white L crystals: white, D crystals: blue

C. Viedma: Cond-mat/040749.

A route to complete chirality of $NaClO_3$

- Change of enantiomeric excess by continuous stirring and abrasion of $NaClO_3$ crystalites in a supersaturated solution

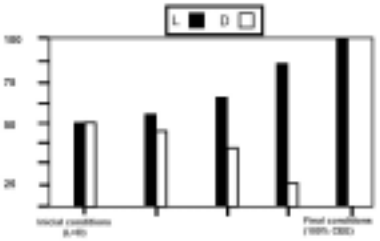


Slight asymmetry results in complete asymmetry.

C. Viedma: Cond-mat/040749.

Recent experiment : a route to complete chirality

- Change of enantiomeric excess by continuous stirring and abrasion of $NaClO_3$ crystalites in a supersaturated solution



Symmetric mixture also acquires complete chirality.

C. Viedma: Cond-mat/040749.

Can we make a consistent model for the nucleation and the chirality conversion?

Important fact in the experiment

- The system is uniform because of the stirring.
- The large crystals are always broken into pieces because of the abrasion.
- There must be a self-amplifying process.
- The minority spices must be eaten up by the majority. (No minority can survive in a niche.)

Elementary processes: 5 component model

- Formation of chiral units: $Z+Z \rightarrow X_u$, $Z+Z \rightarrow Y_u$
- Decay of chiral units: $X_u \rightarrow Z+Z$, $Y_u \rightarrow Z+Z$
- Formation of critical nuclei: $X_u+X_u \rightarrow X$, $Y_u+Y_u \rightarrow Y$
- Growth of crystals: $X+Z \rightarrow X$, $X+X_u \rightarrow X$, $Y+Z \rightarrow Y$, $Y+Y_u \rightarrow Y$
- Decay of crystals: $X \rightarrow X+Z$, $X \rightarrow X+X_u$, $Y \rightarrow Y+X$, $Y \rightarrow Y+X_u$

Z: achiral molecule, X: right-handed crystal, X_u: right chiral unit, Y: left-handed crystal, Y_u: left chiral unit,

Change of masses of the chiral crystals

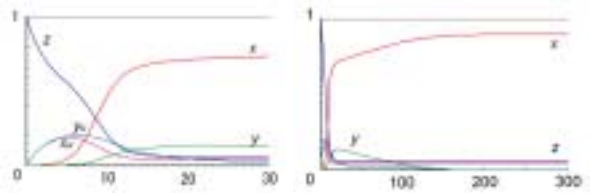
- Masses of the right and left crystals: x and y
- Masses of the right and left chiral units: x_u and y_u
- Mass of achiral molecules: z

$$\frac{dx}{dt} = k_1 z x + k_u x_u x + k_c x_u^2 - \lambda_1 x - \lambda_0 x,$$
$$\frac{dy}{dt} = k_1 z y + k_u y_u y + k_c y_u^2 - \lambda_1 y - \lambda_0 y,$$
$$\frac{dx_u}{dt} = k_0 z^2 - k_u x_u x - k_c x_u^2 + \lambda_0 x - \lambda_0 x_u,$$
$$\frac{dy_u}{dt} = k_0 z^2 - k_u y_u y - k_c y_u^2 + \lambda_0 y - \lambda_0 y_u,$$
$$\frac{dz}{dt} = -2k_0 z^2 - k_1 z x - k_1 z y + \lambda_1 x + \lambda_1 y + \lambda_0 x_u + \lambda_0 y_u.$$

- Total mass is conserved: $x + x_u + y + y_u + z = \text{const.}$

Time evolution: seeding (nucleation)

- Initial condition: $x(0)=0.001$, $y(0)=x_u(0)=y_u(0)=0$ (a small amount of seeds of X)
  → Y also appears in the initial stage, but finally disappears.



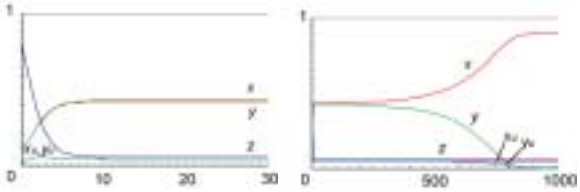
$k_0=0.1$, $k_1=k_u=1$, $k_c=0.01$, $\lambda_0=0.1$, $\lambda_1=\lambda_u=0.05$

M. Uwaha, J. Phys. Soc. Jpn. **73** (2004) 2601

Time evolution: ripening of rasemic mixture

- The initial conditions: x(0)=0.101, y(0)=0.100, $x_u(0)=y_u(0)=0$ (a little excess of X)

  → Y disappears very slowly.



$k_0=0.1$, $k_1=k_u=1$, $k_c=0.01$, $\lambda_0=0.1$, $\lambda_1=\lambda_u=0.05$

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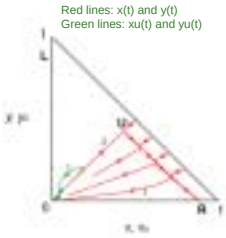
Time evolution—change of masses

- Flow diagram on (x,y) and (x_u,y_u) plane.



Fixed points: (x,y,x_u,y_u,z)

Unstable fixed point
U =(0.429,0.429,0.0412,0.0412,0.059)

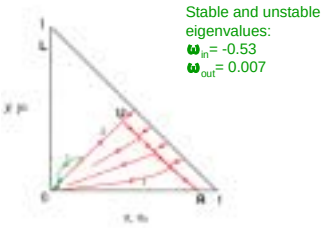
Right-handed crystals
R = ($0.897, 2\times10^{-6}$,0.003, 0.045,0.055)

Left-handed crystals
L = (2×10^{-6},0.897, 0.045, 0.003, 0.055)

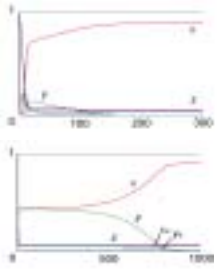
M. Uwaha, J. Phys. Soc. Jpn. **73** (2004) 2601

Time evolution—critical vihavior

- Flow diagram on (x,y) and (x_u,y_u) plane.



Stable and unstable eigenvalues:
ω_{in}= -0.53
ω_{out}= 0.007



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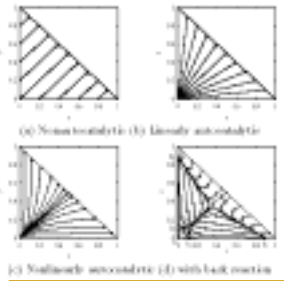
Saito-Hyuga's model for autocatalytic chemical reaction to achieve complete chirality



$$\frac{dr}{dt} = kr^2(1-r-s)-\lambda r$$
$$\frac{ds}{dt} = kr^2(1-r-s)-\lambda s$$

Nonlinear autocatalysis and back reactions are essential to realize complete homochirality.

Y. Saito, H. Hyuga: J. Phys. Soc. Jpn. **73** (2004) 33

Conclusion

- The two experiments can be explained with a simple model consisting of achiral molecule, chiral units and chiral crystals with nucleation via the chiral units.
- The time evolution is divided into two stages: initial fast relaxation and slow change of the enantiomeric excess.
- The chiral units (clusters) may play the crucial role to realize autocatalysis.

Future direction

- The model must be refined and the conditions to realize homochirality in crystallization must be specified more definitely .
- New experiments (different conditions, various materials such as $NaBrO_3$) are wanted.