



# Chiral molecules: a case of spontaneous symmetry breaking?

Giovanni Jona-Lasinio

*Laboratori Nazionali di Frascati, June 6, 2013*

# At the beginning of the story

L. Pasteur *La dissymétrie moléculaire*, 1883

*“...quand le principes immédiats essentiels à la vie prennent naissance, c’est sous l’influence de forces dissymétriques et c’est pourquoi la vie fait des substances dissymétriques.....Me demanderez vous: quelles sont donc le forces dissymétriques qui président à l’élaboration des principes immédiats naturels? Il me serait difficile de répondre avec précision; mais la dissymétrie je la vois partout dans l’univers.... Imaginez le système solaire placé devant una glace, avec le mouvement propre des astres, vous aurez dans la glace una image non superposable à la réalité.”*

# Homochirality

M. Mauksch, S. B. Tsogoeva, *Life's Single Chirality: Origin of Symmetry Breaking in Biomolecules*, in *Biomimetic Organic Synthesis*, eds E. Poupon and B. Nay, Wiley, 2011.

*"Life on earth is based on chiral molecules: amino acids (as constituents of the proteins coded by RNA), sugars, and achiral nucleobases that form together the polymeric nucleic acids (RNA and DNA) as carriers of the genetic code. Both sugars and amino acids are chiral molecules with one or more chiral carbon centers. The absolute configuration of all the amino acids and sugar molecules employed in the molecules of life on earth is almost exclusively uniform: L for amino acids and D for sugars a fact called biological homochirality."*

*"It appears widely accepted now that life as we know it would not be conceivable without the homochirality of biomolecules . Both left- and right-handed versions of biomolecules would, however, in principle be capable of supporting complex life. This leads us to the question whether the observation of only one form of chiral molecules is due to a deterministic process or is, alternatively, accidental, where both forms might have been present in the initial stages of life and one form had become extinct later on in evolution."*

# The shape of molecules: pyramidal molecules

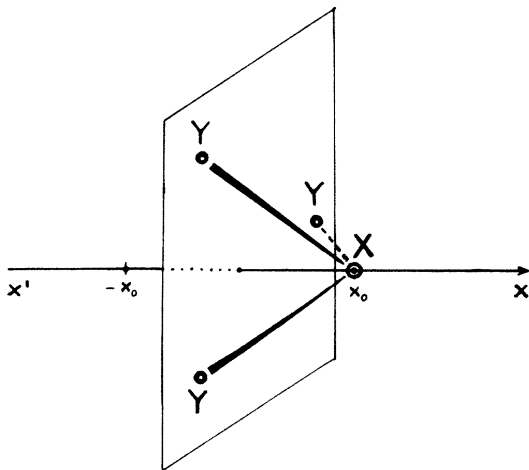


FIG. 1. A pyramidal molecule  $XY_3$  with its inversion axis  $x'x$  and the two nuclear equilibrium configurations  $-x_0$  and  $x_0$ .

# Chiral molecules

Examples of pyramidal molecules are  $NH_3$  ammonia,  $PH_3$  phosphine,  $AsH_3$  arsine. Their chemical symbol is of the form  $XY_3$ .

Suppose that we replace two of the hydrogens with different atoms like deuterium and tritium: we obtain a molecule of the form  $XYWZ$ . This is called an enantiomer, that is a molecule whose mirror image cannot be superimposed to the original one. These molecules are optically active as they rotate the polarization plane of light. For this property they are called chiral.

# Hund's paradox 1927

According to quantum mechanics chiral molecules cannot exist as stationary states.

In fact the corresponding Hamiltonian is invariant under parity and its ground state is necessarily a superposition with equal weights of the two enantiomers. It is therefore delocalized and its dipole moment is zero.

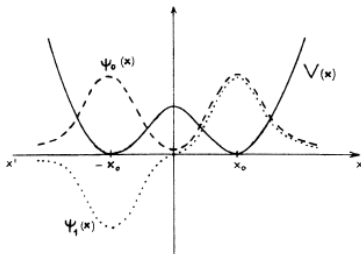


FIG. 2. The one-dimensional symmetric double-well problem. —, potential  $V(x)$ ; — —, ground-state eigenfunction  $\psi_0(x)$ ; . . . , first excited state eigenfunction  $\psi_1(x)$ .



# Could the environment persuade the molecule to become chiral?

## A first proposal

A first mechanism was suggested in the ETH Zürich thesis of P. Pfeifer and can be summarized as follows: take a single molecule and couple it to the quantized transverse electromagnetic field. Then the coupling to the infinite number of soft photons causes a phase transition to two degenerate chiral states for sufficiently small splitting of the inversion doublet of the unperturbed molecule. His calculation was based on a two state approximation for the molecule and the mean field approximation for the resulting spin boson model. H. Spohn and R. Dümcke proved the existence of the phase transition without the mean field approximation but M. Fannes, B. Nachtergaele and A. Verbeure showed that the phase transition disappears at  $T > 0$ . Therefore this mechanism does not seem to provide an explanation.

## A different environment

P. W. Anderson, Phys. Rev. **75**, 1450 (1949); P. Claverie, G. Jona-Lasinio Phys. Rev. A **33**, 2245 (1986)

If we deal with a set of molecules (e.g. in the gaseous state), once localization happens for a molecule there appears a cooperative effect which tends to stabilize this localization. The mechanism is called the reaction field mechanism.

Let  $\mu$  the dipole moment of the localized molecule; this moment polarizes the environment which in turn creates the *reaction field*  $\mathcal{E}$  which is collinear with  $\mu$  and the interaction energy  $V = -\mu \cdot \mathcal{E}$  is negative.

If  $|V| \gg \Delta E$ , where  $\Delta E$  is the doublet splitting due to tunneling in the isolated symmetric state, the molecules of the gas are localized. As a consequence the doublet should disappear when  $|V|$  increases for example by increasing the pressure.

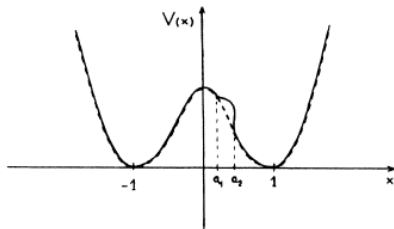


FIG. 3. A symmetric double-well potential with a local perturbation. —, perturbed potential  $V(x) = V_0(x) + V_1(x)$ ; ---, unperturbed potential  $V_0(x)$ . The  $x$  axis has been scaled so that the absolute value  $x_0$  of the minima is equal to 1.

# Tunneling instability in the semiclassical limit

G. Jona-Lasinio, F. Martinelli, E. Scoppola, Comm. Math. Phys. **80**, 223 (1981)

Let us consider a symmetric double well potential  $V_0(x)$ , e.g.  $V_0(x) = V_0(x^2 - 1)^2$  where  $V_0 > 0$  is the height of the barrier separating two minima at  $x = \pm 1$ . Let a perturbing potential  $V_1(x)$  be localized inside one of the wells but possibly away from the minimum. More precisely

$$V_1(x) \neq 0, \quad x \in (a_1, a_2) \subset (0, x^*), \quad V_1(x) = 0 \quad \text{otherwise} . \quad (1)$$

The interval  $(0, x^*)$  includes the minimum at  $x = 1$  and  $(a_1, a_2)$  is a small segment compared to  $(0, x^*)$  so that the perturbation modifies only locally the double well.

Then, essentially independently of the strength of the perturbation, the following estimate holds for sufficiently small  $\hbar/m$ , where  $m$  is the mass of the tunneling particle,

$$\frac{\psi_0(1)}{\psi_0(-1)} \approx -\frac{\psi_1(-1)}{\psi_1(1)} \approx \exp \left[ -\frac{1}{\hbar} \int_{-a_2}^{a_2} (2mV_0(x))^{1/2} dx \right]. \quad (2)$$

Here  $\psi_0(x)$  and  $\psi_1(x)$  denote respectively, the ground state and the first excited state of the *perturbed* problem.

The *independence* of this estimate on the intensity of the perturbation holds provided  $V_1 \gg A \exp[-\frac{C(a_2)}{\hbar}]$  where  $C(a_2) = 2 \int_0^{a_2} (2mV_0(x))^{1/2} dx$  and  $A$  is a pre-factor having the dimension of an energy.

The meaning of this result is that we expect the tunneling atom in a non-isolated pyramidal molecule to be generically localized under semiclassical conditions, that is  $(mV_0)^{1/2}\Delta x/\hbar \gg 1$ , with  $V_0$  the height of the barrier and  $\Delta x$  his width. It is well known that changing the curvature of one of the two symmetric minima produces localisation in the well with the smallest curvature. The above result shows that local much weaker perturbations have the same effect. The sign of  $V_1$  determines the well where localisation occurs.

This argument gives a qualitative account of the different experimental behaviour of  $NH_3$ ,  $PH_3$  and  $AsH_3$  and their substituted derivatives.

From the standpoint of a functional integral description the particle in a double well is like a one-dimensional system of continuous spins and it cannot exhibit a phase transition at finite temperature. Note that in our case  $\hbar$  has the same role as the temperature in statistical mechanics. The phenomenon described however is similar to what happens in the Ising model in  $2d$  below the critical point where it is extremely sensitive to boundary conditions. Boundary conditions, like our local perturbations, act on a space scale small compared to the bulk but are sufficient to drive the system in a state of definite magnetization.

# A mean field model and comparison with experiments

G. Jona-Lasinio, C. Presilla, C. Toninelli Phys. Rev. Lett. **88**, 123001 (2002)

We mimic the inversion degree of freedom of an isolated molecule with the Hamiltonian

$$h_0 = -\frac{\Delta E}{2}\sigma^x, \quad (3)$$

where  $\sigma^x$  is the Pauli matrix in the standard representation with delocalized tunneling eigenstates

$$|1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \quad (4)$$

Since the rotational degrees of freedom of the single pyramidal molecule are faster than the inversion ones, on the time scales of the inversion dynamics the molecules feel an effective attraction arising from the angle averaging of the dipole-dipole interaction at the temperature of the experiment.



In the representation chosen for the Pauli matrices, the localizing effect of the dipole-dipole interaction between two molecules  $i$  and  $j$  can be represented by an interaction term of the form  $\sigma_i^z \sigma_j^z$ , where  $\sigma^z$  has localized eigenstates

$$|L\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |R\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (5)$$

In a mean-field approximation we obtain the total Hamiltonian

$$h(\lambda) = -\frac{\Delta E}{2} \sigma^x - G \sigma^z < \lambda | \sigma^z | \lambda >, \quad (6)$$

where  $|\lambda\rangle$  is the single-molecule state to be determined self-consistently.

The parameter  $G$  represents the dipole interaction energy of a single molecule with the rest of the gas. This must be identified with a sum over all possible molecular distances and all possible dipole orientations calculated with the Boltzmann factor at temperature  $T$ . If  $\rho$  is the density of the gas, we have

$$G = \int_d^\infty \frac{\mu^4}{3(4\pi\epsilon_0\epsilon_r)^2 k_B T r^6} \rho 4\pi r^2 dr = \frac{4\pi}{9} \frac{\mu^4 P}{(4\pi\epsilon_0 k_B T)^2 d^3} \quad (7)$$

where  $\epsilon_r$  is the relative dielectric constant,  $d$  the molecular collision diameter and the fraction in the integrand represents the Keesom energy between two classical dipoles of moment  $\mu$  at distance  $r$ . Equation (7) is valid in the high temperature limit which is appropriate for room temperature experiments.

The coupling constant  $G$  can be estimated, obtaining the same result, also using a different argument which can be easily generalized. This is the reaction field mechanism widely used in physics and chemistry. Let us consider a spherical cavity of radius  $a$  in a homogeneous dielectric medium characterized by a relative dielectric constant  $\epsilon_r$ . An electric dipole  $\boldsymbol{\mu}$  placed at the center of the cavity polarizes the dielectric medium inducing inside the sphere a reaction field  $\boldsymbol{R}$  proportional to  $\boldsymbol{\mu}$

$$\boldsymbol{R} = \frac{2(\epsilon_r - 1)}{2\epsilon_r + 1} \frac{\boldsymbol{\mu}}{4\pi\epsilon_0 a^3}. \quad (8)$$

As a result, the dipole acquires an energy

$$\mathcal{E} = -\frac{1}{2}\boldsymbol{\mu} \cdot \boldsymbol{R} = -\frac{\epsilon_r - 1}{2\epsilon_r + 1} \frac{\mu^2}{4\pi\epsilon_0 a^3} = \frac{4\pi}{9} \frac{\mu^4 P}{(4\pi\epsilon_0 k_B T)^2 d^3}. \quad (9)$$

having used Clausius-Mossotti relation.

The solution of the eigenvalue problem associated to the Hamiltonian (6) gives the following results. If  $G < \Delta E/2$ , there is only one ground state  $\lambda_0 = 1$ , with energy

$$E_0 = -\frac{\Delta E}{2}. \quad (10)$$

If  $G \geq \Delta E/2$ , there are two degenerate ground states

$$|\lambda_0^L\rangle = \sqrt{\frac{1}{2} + \frac{\Delta E}{4G}} |1\rangle + \sqrt{\frac{1}{2} - \frac{\Delta E}{4G}} |2\rangle \quad (11)$$

$$|\lambda_0^R\rangle = \sigma^x |\lambda_0^L\rangle, \quad (12)$$

with energy

$$E_0^L = E_0^R = -\frac{\Delta E}{2} - \frac{1}{2G} \left( \frac{\Delta E}{2} - G \right)^2. \quad (13)$$

By defining the critical value  $G_{\text{cr}} = \Delta E/2$ , for  $G < G_{\text{cr}}$ , the ground state of the system is approximated by a product of delocalized symmetric single-molecule states corresponding to the ground state of an isolated molecule. For  $G \geq G_{\text{cr}}$ , we have two different product states which approximate the ground state of the system.

The corresponding single-molecule states transform one into the other under the action of the inversion operator  $\sigma^x$ , and, for  $G \gg G_{\text{cr}}$ , they become localized

$$\lim_{\Delta E/G \rightarrow 0} |\lambda_0^L \rangle = |L \rangle \quad \lim_{\Delta E/G \rightarrow 0} |\lambda_0^R \rangle = |R \rangle. \quad (14)$$

The above results imply a bifurcation of the ground state at a critical interaction  $G = G_{\text{cr}}$ . Using  $\varrho = P/k_B T$ , this transition can be obtained by increasing the gas pressure above the critical value

$$P_{\text{cr}} = \frac{9}{8\pi} P_0 \left( \frac{T}{T_0} \right)^2, \quad (15)$$

where  $P_0 = \Delta E/d^3$  and  $T_0 = \mu^2/(4\pi\epsilon_0\epsilon_r d^3 k_B)$ .

When the gas is exposed to an electro-magnetic radiation of angular frequency  $\omega_0$ , we add to the Hamiltonian (6) the perturbation

$$h_{\text{em}}(t) = \epsilon f(t) \sigma^z \quad (16)$$

where  $\epsilon$  is a small parameter and  $f(t) = \theta(t) \cos(\omega_0 t)$ ,  $\theta(t)$  being the Heaviside function. The choice of a dipole coupling approximation,  $h_{\text{em}} \propto \sigma^z$ , is justified for a radiation of wavelength long with respect to the molecular size.

The linear response is characterized by the generalized susceptibility

$$\mathcal{R}(\omega) = \frac{2\Delta E}{(\hbar\omega)^2 - (\Delta E^2 - 2G\Delta E)}. \quad (17)$$

This expression has a unique pole at positive frequency which corresponds to the inversion line frequency

$$\bar{\nu} = \frac{\Delta E}{h} \left( 1 - \frac{2G}{\Delta E} \right)^{\frac{1}{2}}. \quad (18)$$

The residue of  $\mathcal{R}(\omega)$  at this pole, namely  $(1 - 2G/\Delta E)^{-1/2}$ , represents the corresponding transition probability.



The theoretical expression (18) for the inversion line frequency can be written

$$\bar{\nu} = \frac{\Delta E}{h} \sqrt{1 - \frac{P}{P_{\text{cr}}}}, \quad (19)$$

where  $P_{\text{cr}}$  is given by

$$P_{\text{cr}} = \frac{9}{8\pi} P_0 \left( \frac{T}{T_0} \right)^2, \quad (20)$$

Note that this expression does not contain free parameters.

We compare our theoretical analysis of the inversion line with the spectroscopic data available for ammonia and deuterated ammonia.

1. B. Bleaney, J. H. Loubster, Nature **161**, 522 (1948), Proc. Phys. Soc. London Sec. A **63**,483 (1950)
2. G. Birnbaum, A. Maryott, Phys. Rev. **92**, 270 (1953)

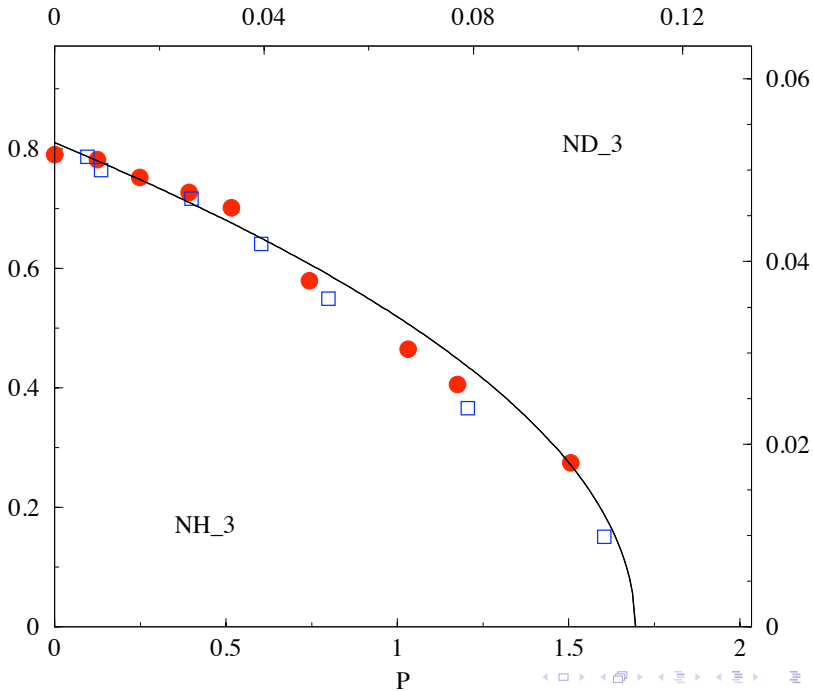
In these experiments the absorption coefficient of a cell containing  $NH_3$  or  $ND_3$  gas at room temperature was measured at different pressures.

The frequency  $\bar{\nu}$  of the inversion line decreases by increasing  $P$  and vanishes for pressures greater than a critical value. There is factor about 15 between the critical pressures of  $NH_3$  and  $ND_3$ .

Equation (19) predicts that, up to a pressure rescaling, the same behavior of  $\bar{\nu}(P)$  is obtained for different pyramidal molecules

$$\frac{\bar{\nu}_{XY_3}(P)}{\bar{\nu}_{XY_3}(0)} = \frac{\bar{\nu}_{X'Y'_3}(\gamma P)}{\bar{\nu}_{X'Y'_3}(0)}, \quad (21)$$

where  $\gamma = P_{\text{cr } X'Y'_3} / P_{\text{cr } XY_3}$ . In the case of  $ND_3$  and  $NH_3$ , at the same temperature  $T$  we have  $\gamma = \Delta E_{NH_3} / \Delta E_{ND_3} \simeq 15.28$ . This factor has been used to fix the scales of the figure. We see that in this way the  $NH_3$  and  $ND_3$  data fall on the same curve.



	$\Delta E$ (cm <sup>-1</sup> )	$\mu$ (Debye)	$d$ (Å)	$T_0$ (Kelvin)	$P_0$ (atm)
NH <sub>3</sub>	0.81	1.47	4.32	193.4	1.97
ND <sub>3</sub>	0.053	1.47	4.32	193.4	0.13
PH <sub>3</sub>	$3.34 \times 10^{-14}$	0.57	–	29.1	$8.11 \times 10^{-14}$
AsH <sub>3</sub>	$2.65 \times 10^{-18}$	0.22	–	4.3	$6.44 \times 10^{-18}$

**Table:** Energy splitting  $\Delta E$ , collision diameter  $d$ , and electric dipole moment  $\mu$ , for different pyramidal molecules. The temperature  $T_0$  and the pressure  $P_0$  are evaluated theoretically. In the case of PH<sub>3</sub> and AsH<sub>3</sub> the collision diameter, not available, is assumed equal to that measured for NH<sub>3</sub> and ND<sub>3</sub>. We used  $\varepsilon_r = 1$ .

# A superselection rule

At pressures greater than the critical one we have the following situation. In the limit of an infinite number of molecules, the Hilbert space separates into two sectors generated by the ground state vectors given in mean field approximation by

$$|\psi_0^L\rangle = |\lambda_0^L\rangle \dots |\lambda_0^L\rangle \quad (22)$$

$$|\psi_0^R\rangle = |\lambda_0^R\rangle \dots |\lambda_0^R\rangle, \quad (23)$$

These sectors, which we call  $\mathcal{H}_{\mathcal{L}}$  and  $\mathcal{H}_{\mathcal{R}}$ , cannot be connected by any operator involving a finite number of degrees of freedom (local operator). This means that a superselection rule operates between the two sectors.

It is natural to define the chirality operator

$$\chi = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N \mathbb{1}_1 \otimes \dots \otimes \sigma_i^z \otimes \dots \otimes \mathbb{1}_N. \quad (24)$$

Then

$$\langle \psi | \chi | \psi \rangle = \pm \sqrt{1 - \left( \frac{\Delta E}{2G} \right)^2} \quad (25)$$

for  $\psi$  in  $\mathcal{H}_L$  and  $\mathcal{H}_R$  respectively, is an order parameter similar to the magnetization.

## Comment

A. S. Wightman, in *Probabilistic Methods in Mathematical Physics*, eds. F. Guerra, M. Loffredo, C. Marchioro, World Scientific 1992; *Nuovo Cimento*, **110 B**, 751 (1995).

*“The theory [of Claverie and Jona-Lasinio] also predicts a superselection rule separating the two chiralities. However, there is an important distinction between this superselection rule and those like the charge.... Here the unobservability of the relative phase is a statement about an observable, the chirality of a single molecule, but it only holds in the presence of an environment.”*



# Spontaneous (dynamical) symmetry breaking

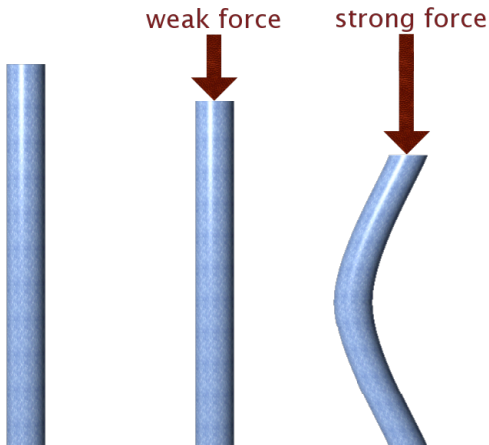


Figure: Elastic rod compressed by a force of increasing strength

# Chiral molecules as a case of SSB

Our model apparently describes a quantum phase transition involving only the inversion degree of freedom of the molecules. A quantum phase transition taking place at room temperature is a novelty and one would like to derive this result from a more realistic model and without the mean field approximation.

A similar treatment can be applied to a gas of pyramidal molecules of very low density in an environment provided by a gas of higher density of molecules of a different kind. In this case one may neglect the interaction among the pyramidal molecules and reduce the problem to a single molecule interacting with the environment.

When the molecules of the environment are not endowed with a dipole moment they can acquire it through deformation under the action of the field of the pyramidal molecules. The localizing effect is much weaker and, for example, in a gas of He the critical pressure for  $NH_3$  is of the order of  $7.3 \cdot 10^3 \text{ atm}$  which is still experimentally accessible in the laboratory.

# Decoherence point of view

*J. Trost, K. Hornberger, Phys. Rev. Lett.* **103**, 023202 (2009).

In a recent work by Trost and Hornberger the existence of chiral molecules is analysed from a dynamical point of view. The basic idea is that an initially localized molecule through repeated scattering in a host gas is blocked in that state (Zeno effect).

The argument is based on the use of the following Lindblad equation equation for the density matrix

$$\partial_t \varrho(t) = \mathcal{L}(\varrho(t)), \quad (26)$$

$$\mathcal{L}(\varrho) = -i \frac{\Delta E}{2\hbar} [\sigma^x, \varrho] - \frac{\gamma}{2} (\varrho - \sigma^z \varrho \sigma^z). \quad (27)$$

This equation is expected to be valid in a dilute gas situation.

For  $\gamma \gg \Delta E/\hbar$  the density matrix  $\varrho(t)$  in the time interval  $1/\gamma \ll t \ll \gamma/(\Delta E/\hbar)^2$  freezes at the value

$$\varrho(t) \simeq \frac{1}{2} (\mathbb{1} + z_0 \sigma^z). \quad (28)$$

Therefore an initially localized state is halted for a time which can be made arbitrarily long depending on the value of  $\gamma$ .

Asymptotically the stationary state is a mixture with equal weights of right-handed and left-handed states that is a racemic mixture. This is contrary to the empirical evidence as in the low density region the doublet is observed which implies delocalized states.

The linear equation cannot explain the shift of the ammonia doublet when the pressure increases. The question naturally arises:

*is it possible to write down a nonlinear evolution equation for the density matrix which includes both the reaction field mechanism and the scattering, that is an equation applicable at higher gas densities and having the correct stationary states?*

So far the SSB interpretation of molecular chirality, besides being conceptually simple, provides for the first time a theory having a qualitative and quantitative support from the empirical data. However one would like to obtain a unified picture.

# Spontaneous symmetry breaking and symmetry restoring in nonequilibrium

M. R. Evans, D. P. Foster, C. Godreche, D. Mukamel, Phys. Rev. Lett. **74**, 208 (1995)

C. Godreche, J. M. Luck, M. R. Evans, D. Mukamel, S. Sandow, E. R. Speer, J. Phys. A **28**, 6039 (1995)

V. Popkov, M. R. Evans, D. Mukamel, J. Phys. A **41**, 432002 (2008)

S. Gupta, D. Mukamel, G. M. Schütz, J. of Phys. A **42** (2009), 485002.

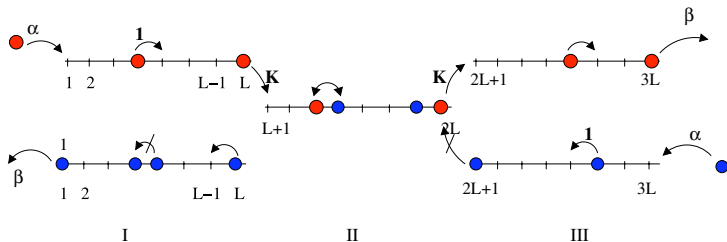
V. Popkov, G. M. Schütz, Phys. Rev. E **86**, 031139 (2012).

V. Popkov, Eur. Phys. J. Special Topics **216**, p. 139 (2013).

SSB has been studied so far mainly as an equilibrium phenomenon typical of systems with infinitely many degrees of freedom. It was discovered however some time ago that out of equilibrium SSB can take place through mechanisms not available in equilibrium.

*Stationary states are the obvious generalization of equilibrium states but the conditions under which SSB takes place in nonequilibrium are different from equilibrium. In stationary nonequilibrium states SSB may be possible even when it is not permitted in equilibrium.*





**Figure 1.** The bridge model with two junctions. Positively (negatively) charged particles hop to the right (left). The model is invariant with respect to left–right reflection and charge inversion. Section II is the bridge. It contains positive and negative particles and holes. Sections I and III comprise parallel segments each containing pluses and holes or minuses and holes.

Summarizing the dynamics, during a time interval  $dt$  three types of exchange events can take place between two adjacent sites

$$+0 \rightarrow 0+ , \quad 0- \rightarrow -0 , \quad +- \rightarrow -+ , \quad (29)$$

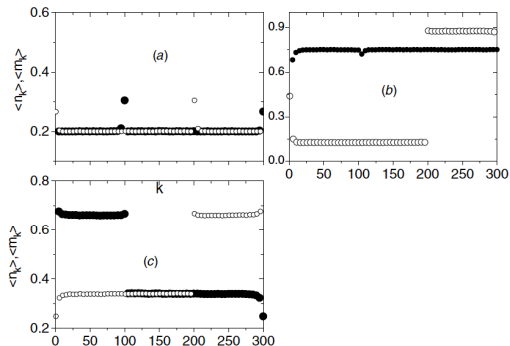
with probability  $dt$ . The last one takes place only on the bridge. At the left of the access lane of plus particles we have

$$0 \rightarrow + , \quad (30)$$

with probability  $\alpha dt$ . At the right end of the exit lane of plus particles

$$+ \rightarrow 0 , \quad (31)$$

with probability  $\beta dt$ , and similarly for minus particles after reflection.



**Figure 3.** Average density profiles for pluses and minuses, from Monte Carlo simulations, in the LDS1 phase (panel (a)), in the SSB phase with pluses majority (panel (b)) and in the LDS2 phase (panel (c)). Pluses (minuses) correspond to closed (open) circles. The system of 300 sites was equilibrated and then, averaging over  $10^6$  Monte Carlo steps was done. Parameters: (a)  $\alpha = 0.2$ ,  $\beta = 0.4$ ; (b)  $\alpha = 0.2$ ,  $\beta = 0.25$ ; (c)  $\alpha = 0.8$ ,  $\beta = 0.9$ .

The existence of two SSB steady states can be easily established in mean field approximation for appropriate values of the rates  $\alpha > \beta$ . The SSB states are connected by the  $CP$  operation.

When the size  $L$  is finite the system flips between the two states. The flipping time  $\tau_{flip}$  can be estimated

$$\tau_{flip} \simeq \exp \kappa L \quad \kappa = 2 \log \frac{\alpha(1 - \alpha)}{\beta(1 - \beta)}$$

# Why is nonequilibrium SSB interesting?

There are facts in the world around us that so far have eluded a really satisfactory explanation.

At the planetary scale we know that in living matter left-handed chiral molecules are the rule.

At the cosmic scale matter is much more abundant than antimatter.

Explanations have been proposed in both cases invoking small symmetry violations which are amplified over a long nonequilibrium evolution to reach the present state.

I suggest to concentrate on the outcome of such evolution rather than on its time trajectory which is anyway very uncertain.

# Biological homochirality

M. Mauksch, S. B. Tsogoeva, *Life's Single Chirality: Origin of Symmetry Breaking in Biomolecules*, in *Biomimetic Organic Synthesis*, eds E. Poupon and B. Nay, Wiley, 2011.

*...several competing theories are vying to explain the origin of bio- logical homochirality, which appears so central to life in the forms we are familiar with. The race between these different approaches is far from decided, as more theories and observations are reported. While some theories for the endogenous origin of homochirality stress a thermodynamic origin of enantioenrichment in the solution phase, others put more weight on mirror symmetry breaking kinetic mechanisms of asymmetric amplification building up upon initial imbalances in the enantiomeric compositions in homogeneous ensembles of chiral molecules..... We have apparently not reached yet a level of understanding of prebiotic chemistry that allows us to decide between alternative explanations.*

# Baryogenesis

M. Shaposhnikov, J. Phys.: Conf. Ser. 171 (2009), 012005.

*Baryogenesis gives a possible answer to the following question: Why there is no antimatter in the Universe? A (qualitative) solution to this problem is known already for quite some time: the Universe is charge asymmetric because it is expanding (the existence of arrow of time, in Sakharov's wording), baryon number is not conserved and the discrete CP-symmetry is broken. If all these three conditions are satisfied, it is guaranteed that some excess of baryons over anti-baryons will be generated in the course of the Universe evolution. However, to get the sign and the magnitude of the baryon asymmetry of the Universe (BAU) one has to understand the precise mechanism of baryon (B) and lepton (L) number non-conservation, to know exactly how the arrow of time is realized and what is the relevant source of CP-violation.*

# What nonequilibrium SSB can do.

G. Jona-Lasinio, Progr. Theor. Phys. **124**, 731 (2010)

The idea is to view biological homochirality and/or baryogenesis as the outcome of a nonequilibrium phase transition.

This means that if the nonequilibrium conditions are such that the stable phase is the SSB phase very small perturbations like parity violating or CP violating forces can drive the system of interest to the stable state avoiding the difficulties of reconstructing a history with many uncertainties.

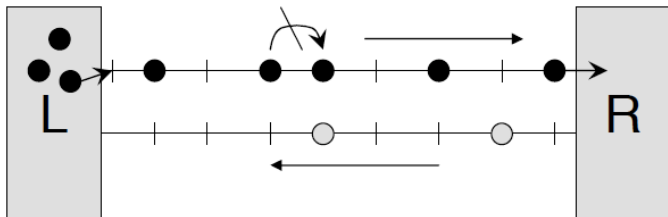
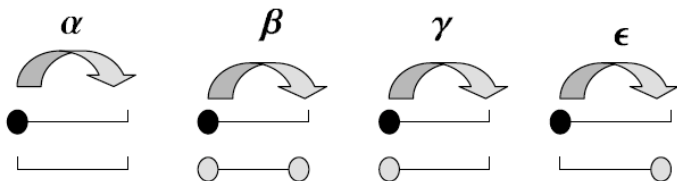
In the case of the Ising model mentioned earlier, below the critical point a single oriented spin is sufficient to drive a macroscopic system to the corresponding ferromagnetic state.



# Is the symmetry breaking only apparent?

V. Popkov, G. M. Schütz, Phys. Rev. E 86, 031139 (2012); V. Popkov, Eur. Phys. J. Special Topics 216, p. 139 (2013).

The following model has been studied by these authors. The dynamics describes particles with repulsive hard-core interaction which hop unidirectionally along two chains of  $L$  sites: One chain for right-hopping particles and another chain for left-hopping particles. At each instant of time the system is fully described by occupation numbers  $n_k$  (for the right movers) and  $m_k$  (for the left-movers). A right-moving particle at site  $k$  can hop to its neighbouring site  $k + 1$  provided it is empty, with a rate that depends on the occupancies at sites  $k, k + 1$  on the adjacent chain.



For values of the interaction in a certain range one observes something very unusual and different. The bulk density profile becomes inhomogeneous and consists of two plateaux with an interface in the middle. The profiles of the two species are left-right symmetric but in each plateau the densities  $\rho_1, \rho_2$  of the left and right movers are different. As the interaction becomes stronger, the difference  $\rho_1 - \rho_2$  grows and reaches the maximum  $\rho_1 - \rho_2 = 0.5$ . Note that the asymmetry of the profile is not a result of a spontaneous symmetry breaking since the profiles are left-right symmetric and the stationary currents of both species remain equal.

