Theory of hierarchical chiral asymmetry

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10.1070/MC2003v013n03ABEH001772

A theory of hierarchical chiral asymmetry based on the sensitivity of symmetry breaking transitions is presented.

Perhaps even more than Louis Pasteur imagined, his famous conjecture, 'L'Univers est dissymétrique', turned out to be true. On all spatial scales, from that of elementary particles to the macroscopic scale of the morphology of mammals, and perhaps of galaxies,[1] nature exhibits a curious asymmetry between the left and the right, which is generally called 'chiral asymmetry'. Yet, most of the fundamental laws show an extraordinary adherence to symmetry. It is only natural to ask, how did these chiral asymmetries at various levels originate? Are they all independent of each other or are they some how related? It is entirely possible that they are all related and it is possible to formulate a general theory of spontaneous generation and propagation of chiral asymmetry from one level to another. This theory will be outlined in this short article.

Spontaneous chiral symmetry breaking under the influence of a bias: To understand the origin of chirally asymmetric states, be they in molecules, micro-tubules or morphology of mammals, we must first note that the physical or chemical states that are generated by natural processes need not reflect process symmetries. Thus, though chemical reactions are chirally symmetric – if we disregard the extremely small violation of this symmetry due to electro-weak interactions – it does not mean that chemical reactions between achiral reactants always generate a racemic product. If there is appropriate chiral autocatalysis and cross inhibition between enantiomers of the product, the process of spontaneous chiral symmetry breaking will generate unequal amounts of the product enantiomers. This fact has been noted by Frank.[2] When cast in the appropriate frame work of thermodynamics, this process can be analysed in a general manner[3,4] and thus a general theory of chiral symmetry breaking could be formulated. As in the case of symmetry-breaking phase transitions, the basic equations of the chiral symmetry breaking system, chemical or otherwise, derive from the two-fold mirror symmetry or parity. The theory has the following variables:

α, a measure of the chiral asymmetry. In chemical systems, α might be the difference between the amount of enantiomers; in other systems it is a similar appropriate measure of the asymmetry;

λ, a parameter, which is a measure of the displacement from a reference state, which is chirally symmetric. In the case of chemical systems, it is a measure of displacement from the state of thermodynamic equilibrium.

In a symmetric state, $\alpha = 0$; in an asymmetric state or a state of broken symmetry, $\alpha \neq 0$; $\alpha > 0$ and $\alpha < 0$ might mean the domination of right- and left-handed structures, respectively. The general theory of spontaneous symmetry breaking gives the following equation for the evolution of α:

$$\frac{d\alpha}{dt} = -A\alpha^3 + B(\lambda - \lambda_c)\alpha. \quad (1)$$

A and B are constants that depend on the particular nature of the systems. In the case of a chemical system, these are constants, which are the functions of kinetic rate constants, and λ_c is a critical value of the parameter λ at which asymmetric states emerge. The steady states ($d\alpha/dt = 0$) of the above equation can be plotted against λ to obtain the so-called 'bifurcation diagram'. Such spontaneous symmetry breaking can be observed in stirred crystallization,[5] for example.

At or close to equilibrium, the steady state $\alpha = 0$, the symmetric state, is stable. This region is represented by the value of $\lambda < \lambda_c$. When $\lambda > \lambda_c$, the symmetric state becomes unstable and the system makes a transition to one of the two asymmetric states, $\alpha > 0$ or $\alpha < 0$, with equal probability.

When there is a small chiral bias that influences the system to make a transition to the state of $\alpha > 0$, for example, the above equation changes to

$$\frac{d\alpha}{dt} = -A\alpha^3 + B(\lambda - \lambda_c)\alpha + Cg + \sqrt{\varepsilon}f(t). \quad (2)$$

Here, the bias is represented by the term Cg; generally, C is a function of the rate constants and g is the dimensionless term that quantifies the strength of the chiral bias. Since the chiral biases are generally small, their influence can be meaningfully analysed only when random fluctuations in α are included. The last term in equation (2) represents random fluctuations with a root-mean-square (RMS) value equal to the square root of ε. With this bias, we can analyse equation (2) as the parameter λ moves through the critical point λ_c according to $\lambda = \lambda_0 + \gamma t$, in which $\lambda_0 < \lambda_c$ is an initial value of λ and t is the time. The result of this analysis is that the probability P_+ with which the system makes a transition to the state $\alpha > 0$ (to which the bias pushes the system) is given by

$$P_+ = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{N} e^{-x^2/2}dx, \quad (3)$$

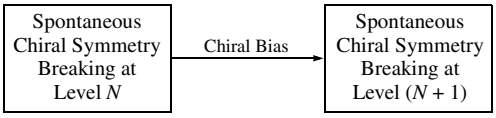
in which

$$N = \frac{Cg}{\sqrt{\varepsilon/2}}\left(\frac{\pi}{B\gamma}\right)^{1/4}. \quad (4)$$

Equation (3) shows that positive chiral biases even smaller than the size of the random fluctuations can profoundly influence the system to evolve to the $\alpha > 0$ state if the rate at which λ sweeps through the critical point γ is very small. This basic theory could act as the basis for understanding the possible relation between chiral asymmetry at various levels. If the system is initially at a value of $\lambda > \lambda_c$, then one can estimate

$$N \approx \frac{Cg}{\sqrt{\varepsilon/2}}\left(\frac{1}{B(\lambda - \lambda_c)}\right)^{1/2} \quad (4)$$

and the bias would have to be larger than the RMS value of random fluctuations for it to have a significant effect.



A theory of hierarchical chiral asymmetry could be based on the above basic theory of the sensitivity of chiral symmetry breaking to small chiral biases. The breaking of chiral symmetry at one level generates a small chiral bias for the next higher level. Chiral bias or asymmetric influence from one spatial scale, 'level N', can thus influence a symmetry breaking transition at a higher level, 'level $(N + 1)$'. We originally proposed this theory to show how parity violating electroweak asymmetry could influence molecular asymmetry in a symmetry breaking transition.[4] Due to the general nature of this theory, it can also be used in many other contexts. For example, recent research suggests that molecular asymmetry is the origin of morphological asymmetry.[6] The coupling between the two scales

occurs through the asymmetric motion of molecular motors. That asymmetry, in turn, must have its origin at the level of amino acids. With an appropriate analysis, it should be possible to obtain an equation of the above form for this system.

Another example is the relation between the chirality of micro-tubules and the chirality of the molecules that self-assemble into micro-tubules:[7,8] for some systems, there is a strong correlation between the chirality of the molecules and the chirality of the micro-tubules, for others the correlation is unobservable. The above theoretical framework could be used to understand the link or its lack. Also, it was reported recently that a vortex motion could have an influence on the chiral symmetry breaking aggregation of molecules into chiral assemblies.[9] Here, the link is between macroscopic vorticity and molecular aggregation. Since the chiral effect of macroscopic vorticity on the molecular scale is extremely small, this phenomenon could be an example of sensitivity in chiral symmetry breaking transition described by the above theory. We may expect to see more such phenomena that relate one scale to another in the future, to which the above theory is applicable. In each system, the constants A, B, C and g have to be evaluated for a careful quantitative study.

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Received: 22nd April 2003; Com. 03/2098