

Model for a cooperative structure wave

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Summary

Cooperativity in water interactions is used to construct a model predicting that both structure and energy are propagated through the liquid in the form of sinusoidal waves.

Cooperativity in water links the concepts of structure and energy. The non-additivity of the hydrogen bond means that ordered regions induce energetically favourable bonding with neighbouring molecules facilitating the structure building process. Thus, we do not consider local changes as resulting from random fluctuations, but as taking definite quantifiable values. We introduce $s(x, t)$ to represent the density of structure at position x and time t . Assuming structure building is proceeding at x as depicted in Figure 1, we have the incremental increase

$$\Delta s = -(ds/dx) \cdot \Delta x \quad (1)$$

and s becomes the dashed curve. The reaction thus appears like a polymerization travelling at that moment from left to right with velocity $c(s) = \Delta x/\Delta t$, allowing us to write s in terms of t

$$\Delta s = -(\partial s/\partial x) \cdot c \cdot \Delta t \quad (2)$$

Defining now another density function $\epsilon(x, t)$ associated with the energy liberated by structure formation, whereby for small changes $\Delta \epsilon = \sigma \cdot \Delta s$, we can use Equation (2) to link s and ϵ

$$(\partial \epsilon/\partial t) = -\sigma \cdot c \cdot (\partial s/\partial x) \quad (3)$$

We can also regard s as the degree of a chemical reaction since its change measures a redistribution of bonds. This reaction is viewed as happening at or close to equilibrium and hence, in the language of irreversible thermo-

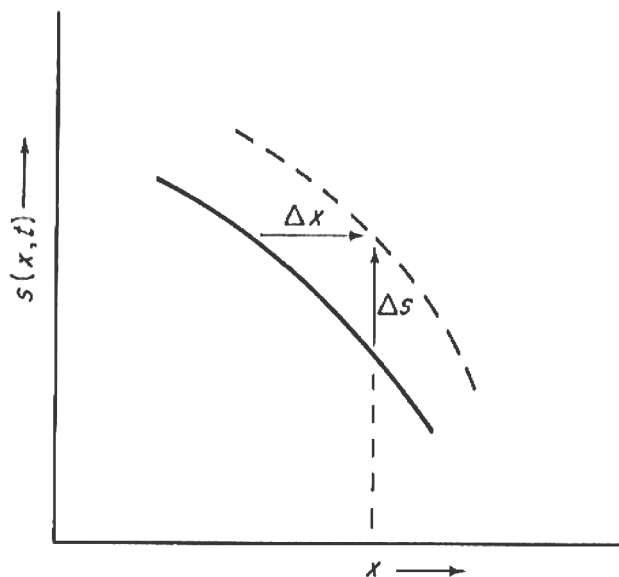


Figure 1 Schematic representation of how the structure function $s(x, t)$ appears to move with velocity $c = \Delta x / \Delta t$. Assuming there is local build-up occurring, then molecules to the left which already have a high degree of order promote structuring on the right via the cooperative interactions and so the process travels in the positive x -direction

dynamics, its rate can be equated to an affinity or potential difference between products and reactants. The values of s at x and $x - \Delta x$ represent the reactants and products, provided the reaction is proceeding as depicted in Figure 1, and over the same distance the potential drop is $(d\varepsilon/dx) \Delta x$, and the reaction rate in the small volume Δx is

$$(\partial s / \partial t) = -\gamma \cdot (\partial \varepsilon / \partial x) \quad (4)$$

This equation has the form of a phenomenological equation where the 'flux' ds/dt is set proportional to the driving 'force' $-(d\varepsilon/dx)$.

Combining Equations (3) and (4) leads directly to the classical wave equations

$$\frac{\partial^2 \varepsilon}{\partial t^2} = c^2 \cdot \frac{\partial^2 \varepsilon}{\partial x^2} \quad \frac{\partial^2 s}{\partial t^2} = c^2 \cdot \frac{\partial^2 s}{\partial x^2} \quad (5)$$

provided the velocity can be expressed as $c = \sigma \cdot \gamma$. This result implies that both structure and energy are transmitted as waves in a medium where the mechanism of intermolecular interactions is cooperative.

The exact form that a structure wave would take is an open question, so for discussion we take the simplest stationary sinusoidal form

$$\varepsilon = 2 \cos(kx) \cos(\omega t) \quad s = 2 \sin(kx) \sin(\omega t) \quad (6)$$

where $k = 2\pi/\lambda$, $\omega = 2\pi\nu$ and $\lambda\nu = c$. In wave motion of this type the energy is not given directly by the oscillation but by its quadratic form, so we introduce two new density functions

$$E = 4a \cos^2(kx)\cos^2(\omega t) \quad I = 4b \sin^2(kx)\sin^2(\omega t) \quad (7)$$

As the wave passes it causes changes in $E \, dx$ and $I \, dx$, i.e. the local energy and structure content in the small volume dx . After introducing a factor T to equalize the amplitudes, $a = bT$, we can add these changes together to obtain another oscillating function

$$\frac{\partial E}{\partial t} + T \frac{\partial I}{\partial t} = -4\omega bT \cos(2kx)\sin(2\omega t) \quad (8)$$

This represents another local change and, if taken as a displacement wave describing the to and fro motions of the water molecules accompanying the fluctuations in E and I , it is simply the local volume change. This new wave has the form

$$y = -2Y \sin(2kx)\cos(2\omega t) \quad (9)$$

whereby small volumes change with the rate $d(dy/dx)/dt$. This argument allows us to identify Equation (8) with the thermodynamic statement, $dE = T \, dS - P \, dV$, connecting changes in internal energy, entropy and volume. This condition for the wave motion prescribes that the wavelength is proportional to the ratio P/T since it follows

$$\lambda = \frac{4\pi Y}{b} \cdot \frac{P}{T} \quad (10)$$

From Equation (7) b is an amplitude giving the maximum density of order or structure building centres. Considering the ratio P/T as a measure of the density of degrees of freedom, then Equation (10) tells us that the wave has longer wavelengths in systems where there are more degrees of freedom per ordering centre. This picture seems reasonable, since it predicts that local order extends over a larger region, i.e. we have bigger clusters or networks, when there are more modes of interaction available to each building centre.

Another consequence of Equation (8) is that the changes in the function I represent negative changes in entropy. The work of Brillouin has established this form of function, the so-called negentropy, in theoretical physics. It is built around the idea that at the molecular level negative entropy can be identified with information. We are thus led to the conclusion that information can be transmitted through an aqueous medium without requiring a permanent covalently linked structure. It also provides us with a thermodynamic definition of the variable $s(x, t)$ which was introduced in quite a different way in Figure 1. On the other hand, $e(x, t)$ being the square root of

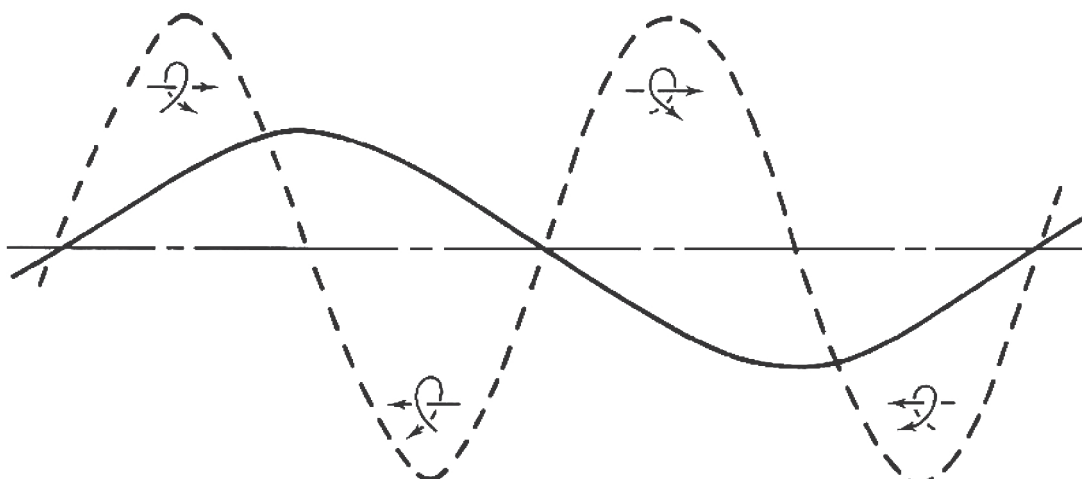


Figure 2 Regions of defined molecular rotations and translations according to $\varepsilon(x,t)$ (solid curve) and $y(x,t)$ (dashed curve). In each of the four half-wavelengths of y is a different combination. $s(x,t)$ shown by the broken curve is taken to be zero at this moment, $\sin(\omega t) = 0$

energy, is a more familiar quantity. It probably represents the momentum associated with rotations, as the molecules reorientate to fit into or break away from ordered clusters. Their translations are given by Equation (9), which in combination with these proposed rotations $\varepsilon(x,t)$, are depicted in Figure 2.

Within the bulk of liquid water we cannot expect any preferred direction of propagation. The build-up and break-down of structured regions should then appear as random clustering and molecular cross-linking as randomly percolated hydrogen bonding. But a solute-solvent interface might force direction and order into these fluctuations. The living cell abounds in regions of layered membrane systems and the aligned protein filaments of the cytoskeleton in registered arrays. These macroscopic structures present networks of parallel interfaces to the solvent medium, so that, assuming they impose direction on the structure wave, the entire region is filled with the solvent medium fluctuating in a concerted way.

The wave model depicts how cooperativity could have far-reaching influence which operates without the existence of an interposed covalently bonded structure. It does not predict the molecular details of any structure, as do computer simulations, but it does predict that they repeat themselves periodically over larger distances and that structural changes can be transmitted beyond the local region of their occurrence. Such a mechanism may underlie the observations of long-range effects seen even in the absence of detectable ordering in the intervening solvent medium.