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PROTEINS IN THE EXPERIMENT *

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ABSTRACT

The backbone of ferredoxin and hemoproteins are described by SAWs in two and three dimensions. But the spin-lattice relaxation process of Fe^{3+} ions cannot be described by pure fractal model. The spectral dimensions observed in experiment is defined through $d_s = d_f/a$, a is given by the scaling form of the low frequency mode $\omega(bL) = b^a \omega(L)$ of the whole system consisting of proteins and the solvent upon a change of the length scale.

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For temperature $T \gg g\,\mu_B H/k$, the spin-lattice relaxation of Fe^{3+} ions in low-spin ferredoxin and hemoproteins is dominated by a two-phonon process (Raman). The temperature dependence of the relaxation time τ is given by (Orbach 1961; Allen et al. 1982)

$$1/\tau \propto T^{3+2d_s} F(T/\theta, d_s) \quad , \tag{1}$$

where $F(x,y)$ is a smooth function of x, and θ is the Debye temperature. The fracton or spectral dimension d_s (Alexander et al 1982; Rammal et al 1983) enter Eq.(1) through

$$\rho(\omega) \propto \omega^{d_s - 1} \quad , \tag{2}$$

where $\rho(\omega)$ is the phonon density of states at low frequencies and ω is the frequency. For an ordinary d-dimensional object, d_s coincides with the Euclidean dimension d, and Eq.(1) is in good agreement with experiment.

However, experiment (Allen et al 1982; Mailer et al 1973; Stapleton et al 1980; Colvin et al 1985) shows that d_s and the fractal dimension d_f are 4/3 for ferredoxin and 5/3 for hemoproteins. Some authors (Mailer et al 1973; Allen et al 1982)identified d_s with the fractal dimension d_f and postulated the validity of Eq.(1) also for noninteger value of d_s. As these values coincide with the fractal dimensions for two and three dimensional self-avoiding walks (SAWs), they also argued that the protein backbones can be modelled by SAWs. However, the spectral dimension d_s is in general different from the fractal dimension d_f and the space dimension d (Stanley 1984). For SAWs, $d_s = 1$. The substitution $d_s = 1$ into Eq.(1) gives a result which disagrees with experiment.

To resolve this conflict, Helman et al (1984, 1985) proposed a fractal model which incorporated massless bridges. They argued that for a high enough density of the bridges, d_s equals d_f. But theoretical analysis (Cates 1985; Stapleton 1985) and computer simulations (Yang et al 1985; Chowdhury et al 1985) shows that the inclusion of finite length bridges do not change the spectral dimension of the system.

I think that the disagreement between theory and experiment is because the previous theory was based on "pure" fractal models, but the experiment was done

in the solvent (water). The phonon density of states is different for these two cases. Physically, the relaxation process involves a modulation of the orbital electronic wave function by structural vibrations. The spins are coupled to vibrations via spin-orbit interactions. Therefore, only those phonon modes that affect the orbital wave function of F_e^{3+} ions contribute to the relaxation process. In this letter, I propose a fractal model that incorporates the solvent effect. The protein molecules, and therefore F_e^{3+} ions form self-avoiding walk configurations on the lattice, the other sites are occupied by solvent molecules, Fig.(1). Only when the distance between F_e^{3+} ions changes can the spins flip, only the vibrational modes in the F_e^{3+} ions contribute to the relaxation process. Following the scaling argument given by Rammal and Toulouse (Rammal, Toulouse 1983), under a change of the length scale $L \to bL$, the number of F_e^{3+} ions in an unit volume changes as

$$N(L) = b^{-d_f} N(bL) \quad , \tag{3}$$

where d_f is the fractal dimension of the protein. Assume the protein backbones to be SAWs, $d_f = (d+2)/3$. If under this scale transformation, the mode frequency has also a scaling behavior

$$\omega_L = b^{-a}\omega_{bL} \tag{4}$$

as the number of phonon modes related to F_e^{3+} ions is proportional to the number of the ions, denoting $\rho(\omega)$ as the density of states of phonons which are related to the F_e^{3+} ions, it follows

$$\rho_L(\omega_L) = b^{-d_f}\rho_{bL}(\omega_{bL})\frac{d\omega_{bL}}{d\omega_L} = b^{a-d_f}\rho_{bL}(\omega_{bL}) \quad . \tag{5}$$

Taking $b = \omega^{-1/a}$, it is easily seen that the spectral dimension is given by

$$d_s = d_f/a \quad . \tag{6}$$

From the presentation given above, one sees that the solvent effect is reflected in the scaling form of the mode frequency, Eq.(4). If protein-protein, protein-solvent, solvent-solvent interactions are the same, the vibrational spectrum is just the same as that of a homogeneous system, i. e. a=1. It is conjectured that if all the three interactions are finite, one also has a=1. This is just the case with the experiment, and the agreement between theory and experiment is restored. If the interactions between molecules are isotropic,then the equations of motion of the system are

$$m_i\frac{d^2u_i}{dt^2} = \sum_\delta K_{i,i+\delta}(u_{i+\delta}-u_i) \tag{7}$$

where i denotes the type and the position of the atoms. $K_{i,j}$ is the force constant between atom i and j. m_i is the mass of atom i. δ is the nearest neighbour vector. Fourier transform of Eq.(7) is

$$-\omega^2 m_i u_i = \sum_\delta K_{i,i+\delta}(u_{i+\delta}-u_i) \quad . \tag{8}$$

Recall the Laplace transform of the master equation for the random walk problem

$$-\varepsilon p_i = \sum_\delta W_{i,i+\delta}(p_{i+\delta}-p_i) \quad , \tag{9}$$

where $p_i(t)$ is the probability that the walker is at position i at time t, $W_{i,j}$ the jump probability from i to j. If the average distance travelled by the random walker at time t has the scaling form

$$R(t) \propto t^{1/d_w} \quad . \tag{10}$$

From the similarity of Eq.(8) and Eq.(9), the following relation exists (Alexander et al 1982, Rammal et al 1983)

$$a = d_w/2 \tag{11}$$

Transformed from vibrational problem to random walk problem, the jump probability $W_{i,j}$ are dependent on i and j, but all are finite. Therefore, a finite lower bound W_{min} and a finite upper bound W_{max} exist. Denote $R_{min}(t)$ as the mean distance travelled by the random walker at time t with all jump probabilities equal W_{min}, and $R_{max}(t)$ with all jump probabilities equal W_{max}, it follows

$$R_{min}(t) \leqslant R(t) \leqslant R_{max}(t) \quad . \tag{12}$$

Since

$$\begin{aligned} R_{min}(t) &\propto t^{1/2} \\ R_{max}(t) &\propto t^{1/2} \end{aligned} \tag{13}$$

it follows

$$R(t) \propto t^{1/2} \quad . \tag{14}$$

This proves the conjecture given above for the isotropic interactions.

In conclusion one cannot explain the experimental results for ferredoxin and hemoproteins by pure fractal model. The spectral dimension observed in experiment is in general different from that of the pure fractal model. One should be careful while applying the results from pure fractal model to real physical systems.

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Lattice model for proteins in the solvent. Sites linked by the heavy lines are proteins molecules and they form self-avoiding walk configurations. Other lattice sites are occupied by the solvent molecules.

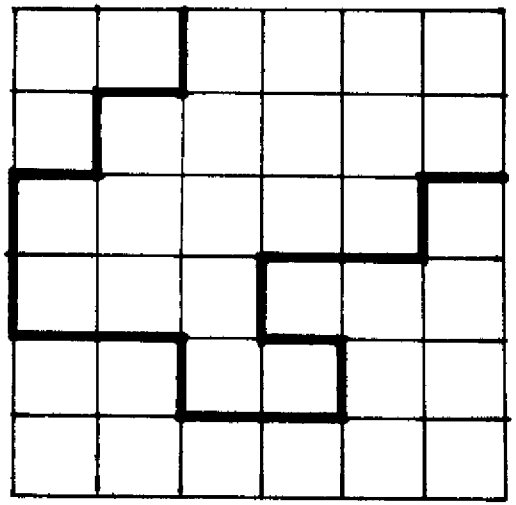

Fig.1