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LETTER TO THE EDITOR

# On lysozyme as a possible high-temperature superconductor

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**Abstract.** Intensity autocorrelation measurements of the diffusion constant of lysozyme molecules in aqueous solutions as a function of applied magnetic field reveal no evidence of the cooperative behaviour proposed by Ahmed, Calderwood, Fröhlich and Smith to explain their observation of a large peak in the diamagnetic susceptibility of lysozyme at an applied field of 600 Oe. Careful susceptibility measurements using a SQUID system show that the diamagnetic susceptibility of lysozyme and lysozyme solutions is constant up to our maximum field of 720 Oe.

Ahmed *et al* (1975, 1976) have measured the magnetic susceptibility and dielectric constant of dilute aqueous solutions of lysozyme, and of lysozyme powder itself. As the value of the magnetic field was raised to about 600 Oe, they observed that the magnitude of the diamagnetic susceptibility, $|\chi|$, increased dramatically. With a further increase in field, $|\chi|$ fell sharply to a constant baseline value. Although the magnitude of the jump in $|\chi|$ depended upon many factors, such as the lysozyme concentration and the pH of the solution, the peak in $|\chi|$ always appeared at about 600 Oe. Ahmed *et al* proposed a model in which each lysozyme molecule has a small superconductive region associated with it. In the presence of a magnetic field the system gains free energy by the formation of lysozyme molecular clusters, leading to a large increase in $|\chi|$. The sudden drop in $|\chi|$ above 600 Oe was interpreted as a manifestation of the Meissner effect.

Because of the potential significance of this work in terms of the possible existence of high-temperature molecular superconductivity, we carried out scattered-light intensity autocorrelation studies of the behaviour of the diffusion constant of lysozyme molecules as a function of magnetic field. Recent light-scattering work on solutions of interacting macromolecules (Doherty and Benedek 1974) has demonstrated that this technique provides a sensitive indicator of collective molecular behaviour. In addition, we measured the magnetic susceptibility of lysozyme at room temperature in magnetic fields up to 720 Oe in an effort to reproduce the published results of Ahmed *et al*.

The lysozyme used in our work was obtained from Sigma Chemical Company (3x dialysed and crystallized, Grade I) who also supplied the lysozyme used by Ahmed *et al*. Four different samples of lysozyme were made up, largely in an effort to duplicate a selection of the sample configurations used by Ahmed *et al*: sample 1, lysozyme powder; sample 2, 'humid' lysozyme made by mixing roughly equal parts of lysozyme and water;

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sample 3, a 0·8% (weight) solution of lysozyme in an aqueous 0·1 m acetate buffer at pH = 5·0; and sample 4, a 1·6% solution of lysozyme in an aqueous 0·1 m acetate buffer at pH = 4·2. This last solution was filtered through a 500 Å millipore filter which reduced the lysozyme concentration to 0·8% before it was used in any measurements.

In our first set of measurements, we measured the diffusion constant of the lysozyme molecules as a function of magnetic field using intensity autocorrelation techniques.

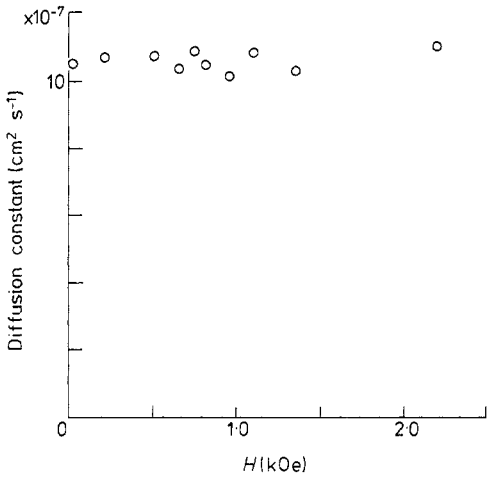


**Figure 1.** Measured diffusion constant of lysozyme molecules in a 0·8% (weight) aqueous solution with pH = 4·2 (sample no 4) as a function of magnetic field.

It was found that, in order to get an exponential intensity autocorrelation function, indicating a monodisperse size distribution, and to have our zero-field measurements agree with previous measurements of both the diffusion constant and molecular weight (Dubin 1972), we had to filter the solution of lysozyme through a 500 Å pore size filter. This is our sample no 4. The sample was placed between the poles of an electromagnet. A beam from an argon ion laser operating at $\lambda = 5145$ Å was directed into the scattering cell perpendicular to the magnetic field with polarization parallel to the field. Light scattered at 90° to both the incident beam and the magnetic field was then analysed with an autocorrelator (Lyons *et al* 1974). The diffusion of the lysozyme molecules was determined from the decay time of the quite-exponential intensity autocorrelation function. The diffusion constant versus magnetic field is plotted in figure 1. As can be seen, there is no dependence of the diffusion constant on the magnetic field to 2·2 kOe, implying that no collective motion of the lysozyme molecules develops as a function of magnetic field. Our zero-field value for the diffusion constant of lysozyme normalized to 20°C is $D = (10{\cdot}5 \times 10^{-7}) \pm 1\%\ \mathrm{cm^2\ s^{-1}}$, which agrees with the zero-field value given by Dubin (1972) to within 1%. The sample temperature varied from 23·5°C to 24·5°C during the measurements.

Our second series of measurements consisted of measuring the magnetic susceptibility of the samples as a function of magnetic field.

A magnetometer system consisting of a superconducting flux transformer coupled to a SQUID (superconducting quantum interference device) and containing a superconducting solenoid capable of providing DC fields up to 720 Oe was used in these measurements.

A re-entrant dewar allowed measurements to be made at room temperature. The sample cell was made from five-ninths pure copper (approximately 0·6 ppm iron) with a bulk room-temperature susceptibility of $\chi = (-8{\cdot}27 \pm 0{\cdot}08) \times 10^{-8}$ emu g$^{-1}$. The susceptibility of our sample container after machining was measured to be $\chi = (-8{\cdot}2 \pm 0{\cdot}1) \times 10^{-8}$ emu g$^{-1}$. No magnetic remnance was detected. The temperature varied between 21°C and 17°C from the beginning to the end of a run. At the end of each run,

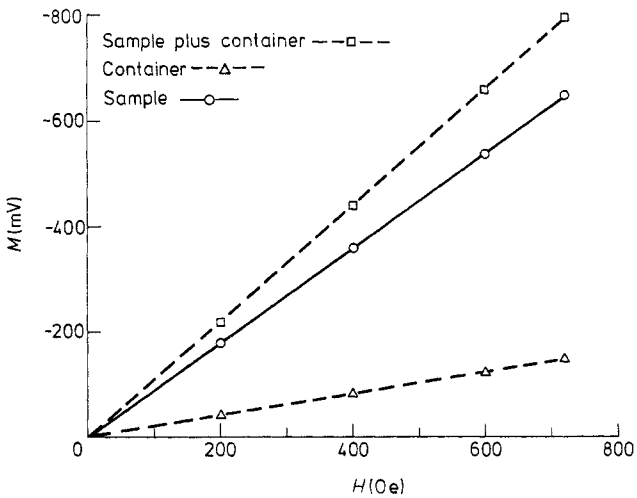


**Figure 2.** Magnetic moment (in mV) of sample no 4 versus magnetic field. To determine the susceptibility, the measured $M$ value of the empty container is subtracted from that of the filled container at each field value studied ($H$ = 200, 400, 600 and 720 Oe). These results are then divided by $H$(Oe) times the mass of the sample, multiplied by the system calibration $1{\cdot}36 \times 10^{-7}$ emu mV$^{-1}$ and averaged to get the result $\chi = -7{\cdot}1 \pm 0{\cdot}2$ emu g$^{-1}$.

the magnetization corresponding to a starting-field value was remeasured and no significant temperature dependence was found. The resulting $M$ versus $H$ behaviour for sample no 4 is shown in figure 2. The linearity of the plot indicates a constant $\chi$ for the range 0–720 Oe. Similar data were recorded for each of the other samples. Table 1 is a summary of our susceptibility measurements. The dominant contribution to the inaccuracy of our $\chi$ values in the table is the error associated with weighing the small amounts of sample used, particularly in the cases of the dry and 'humid' lysozyme samples. However, in comparing the magnetization values for the same specimen at different field points, only the *precision* of the SQUID system is relevant, and that is ~2%. In no instance did the 600 Oe value deviate by more than this amount from the average susceptibility of the sample.

**Table 1.**

| Sample | Mass (g) | $\chi$ (emu g$^{-1}$) |
|---|---|---|
| 1 (dry lysozyme) | 0·019 | $(-6{\cdot}0 \pm 0{\cdot}5) \times 10^{-7}$ |
| 2 (humid lysozyme) | 0·017 | $(-8{\cdot}1 \pm 0{\cdot}7) \times 10^{-7}$ |
| 3 (0·8%, pH = 5·0) | 0·131 | $(-7{\cdot}0 \pm 0{\cdot}3) \times 10^{-7}$ |
| 4 (0·8%, pH = 4·2) | 0·172 | $(-7{\cdot}1 \pm 0{\cdot}2) \times 10^{-7}$ |

In conclusion, our light-scattering measurements on a lysozyme solution lead to a value of the diffusion constant in agreement with that of Dubin (1972) and reveal no evidence of molecular clustering or collective molecular activity as a function of magnetic field. Our measurements of the magnetic susceptibility of various samples of lysozyme and lysozyme solutions show no indication of an anomalous diamagnetic susceptibility up to magnetic fields of 720 Oe. This latter result is in sharp contrast with the published results of Ahmed *et al* (1975, 1976).

We thank Dr F P Milanovich for bringing the work of Ahmed *et al* to our attention.

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