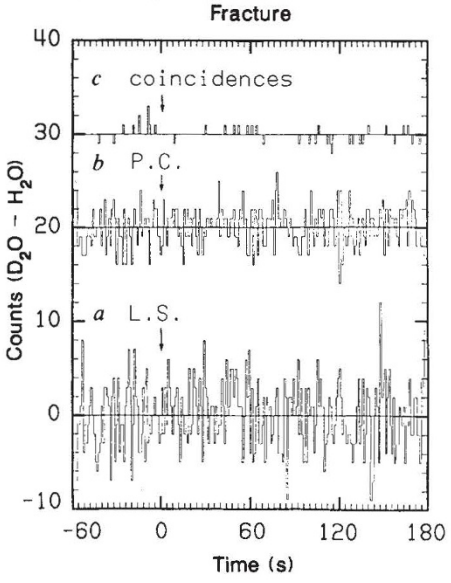
Fracture without fusion

SIR—Several years ago, Derjaguin *et al.*[1] claimed that the fracture of D_2O by macroscopic projectiles with moderate velocities induces d + d fusion. The evidence, scant at best, was based on detecting pulses in a BF_3 proportional counter array, in coincidence with the macroscopic impacts, in excess of the numbers observed using H_2O targets. More recent work by the same group claims that fusion also occurs in mechanically agitated mixtures of titanium in the presence of deuterium[2]. These intriguing claims gain some credibility from studies of exoelectrons[3,4] which indicate that a significant fraction of the electrons emitted on the fracture of certain materials have energies exceeding 1 keV. Thus, Dickinson *et al.*[4] have found that approximately 15 per cent of the electrons



The difference spectra for 75 shots on D_2O and 75 shots on H_2O. *a*, Singles liquid scintillator; *b*, singles proportional counter array; *c*, coincidence between the liquid scintillator and the proportional counter array. The time of the shots is t=0. *b* and *c* are plotted with offsets of 20 and 30 counts, respectively.

emitted on the fracture of epoxy strands could not be stopped by retarding potentials in the 500–1,000 V range.

The recent work of Beuhler *et al.*[5] on cluster impact fusion may also relate to this problem. Fusion cross-sections, from the impact of deuterated clusters of ice containing a few hundred molecules on targets with a high deuteron density, are substantially greater than would be expected from gas phase reactions with similar nucleus–nucleus velocities.

The works cited above suggest that there is a need for further work to investigate the possible fusion mechanisms which might occur in the fracture of solid targets with high deuteron densities. Because the statistics of the measurements of the shattering of deuterated ice with large projectiles are limited, we have repeated this experiment. Our results have been negative, with an upper limit of the number of neutrons per fracture event which is 15-times less than the positive result of Derjaguin *et al.*[1].

In our experiment, a gas gun propelled steel ball bearings, of mass 0.131 g and diameter 1/8 inch, at $168 \pm 4\ m\ s^{-1}$ at polycrystalline ice. The ice (the D_2O was 99.9 atom per cent D) was frozen in a dry-ice acetone bath at −66 °C. The target was inside the well of a liquid scintillator detector (LS). Neutron pulses in the liquid scintillator were selected by standard 1-dimensional pulse shape discrimination logic. A set of twelve proportional counters (PCs), imbedded in a paraffin cylinder, encircled the target and the liquid scintillator. Pulses from the PCs result from the capture of thermalized neutrons, whereas the pulses from the scintillator result from neutron scattering. Another set of three PCs positioned at a greater radial distance, outside both Cd and B_4C neutron shielding, was used as a guard ring, run in anticoincidence with the main PC ring. The two detector systems (LS and PC) were operated both in singles modes and in coincidence with each other. The efficiencies, background count rates and the upper limits (2σ) to the number of neutrons per shot for the three modes of operation are given in the table.

The results from 75 shots on both D_2O and H_2O are shown in the figure. There is no indication of enhanced count rate at the time of the shot (time=0) or afterwards. Analysis of the spectra yields an upper limit less than 1 neutron per shot (see Table). The work reported in ref. 1 gives a positive result at a level of approximately 10 neutrons per shot, yet as best as we can determine, our experimental conditions are similar in all important details. The limited statistics presented in refs 1 and 2 and our negative results convince us that there is no compelling evidence for fracture induced fusion.

Neutron counter characteristics and results

	LS	PC	LS-PC
Background (counts min^{-1})	5.3	1.6	0.054
Efficiencies with neutrons from			
^{252}Cf (2± 1 MeV)	25(%)	13.8(%)	4(%)
Am-Be (4± 2 MeV)	~20(%)	11.6(%)	4(%)
Upper limit neutrons per shot	0.6	0.8	0.7

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Folding pathway enigma

SIR—Fersht and co-workers recently published an interesting approach to studying the transition state and pathway of protein unfolding[1]. They propose a new way to interpret the kinetics of urea-induced unfolding of wild-type and mutant forms of barnase. They find significant differences in the importance of specific protein regions on the energy level of the transition state for unfolding. Their interpretation is that some regions are already exposed to solvent whereas others, such as the N-terminal helix, still show native-like structure in the transition state.

These experiments provide additional insight into the mechanisms of urea-induced protein unfolding, but they do not necessarily provide information on the transition state and pathway of refolding of proteins as suggested by the authors.

Their data analysis is based on the assumption that barnase exists only in two distinct conformational states: native and denatured. The validity of such a two-state model could only be proven by calorimetric measurements which, to our knowledge, have not yet been carried out.

Also, the thermodynamic cycles proposed in the article (see Fig. 4, ref. 1) are purely hypothetical, as the authors have to assume an equilibrium between wild-type and mutant protein which is obviously out of range of experimental handling.

The main shortcoming, however, is the use of the unfolding kinetic data to elucidate the transition state and pathway of protein folding. This is only legitimate under identical conditions, where the principle of microscopic reversibility is valid, that is, under strongly denaturing conditions. The authors' comparison of their results with recent NMR studies on early refolding steps[2,3] is misleading because these studies were carried out under "strongly native conditions". Under these conditions (as Fersht and co-workers agree) the folding pathway is essentially different from the mechanism of unfolding because partially folded intermediates are formed rapidly in the refolding of many proteins[4–6].