Non Equivalence of the Step and Delta Function in Perturbation Experiments.

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At the last CCP5 meeting we raised the question of equivalence between step and delta function perturbation experiments and provoked some incredulity among members of the audience. We would like to qualify our statements by presenting some data and the germ of an explanation for our results.

The response of an observable $O(\underline{k})$ at wavevector $\underline{k}$, can be related[1] to an equilibrium correlation function $\langle \ \rangle_0$ by,

$$\langle O(\underline{k})\rangle_t = \frac{V}{k_B T}\int_{-\infty}^{t} dt' \langle O(\underline{k},t)\ J(-\underline{k},t')\rangle_0 \ i\underline{k}\phi(\underline{k},t') \qquad (1)$$

where the perturbation $\phi(\underline{k},t)$ couples to a dynamic variable with corresponding current J. The response of the current itself to a delta function perturbation is then just the correlation function ,

$$\langle J(\underline{k})\rangle_t = \frac{V}{k_B T}\langle J(\underline{k},t)\ J(-\underline{k},0)\rangle_0 \qquad (2)$$

while a step function gives the integral,

$$\langle J(\underline{k})\rangle_t = \frac{V}{k_B T}\int_0^t \langle J(\underline{k},t)\ J(-\underline{k},0)\rangle_0\, dt \qquad (3)$$

Integration of the response to a delta function perturbation should therefore be identical to the observed response in a step function experiment.

In figures 1 and 2 we make this comparison at two densities in liquid Cl_2 for the xz component of the stress tensor in response to shear rate perturbations of the same symmetry. These results were obtained by direct subtraction of trajectories rather than by linearising and expanding the equations of motion. Evidently the responses are not identical in that the delta function clearly results in a better signal to noise ratio at long times.This is very desirable, particularly in this instance where the maximum value reached by the response at long times corresponds to the viscosity of the system.

The development of equation (1) rests upon the ergodic theorem in that the angular brackets imply a statistical response obtained by averaging over many pairs of trajectories or'segments'.Thus although we may expect the responses in figs 1 and 2 to converge after a large number of segments have been taken, for the few runs feasible in practice expressions 1-3 are not strictly valid and the detailed response, i.e. the noise, need not be equivalent.

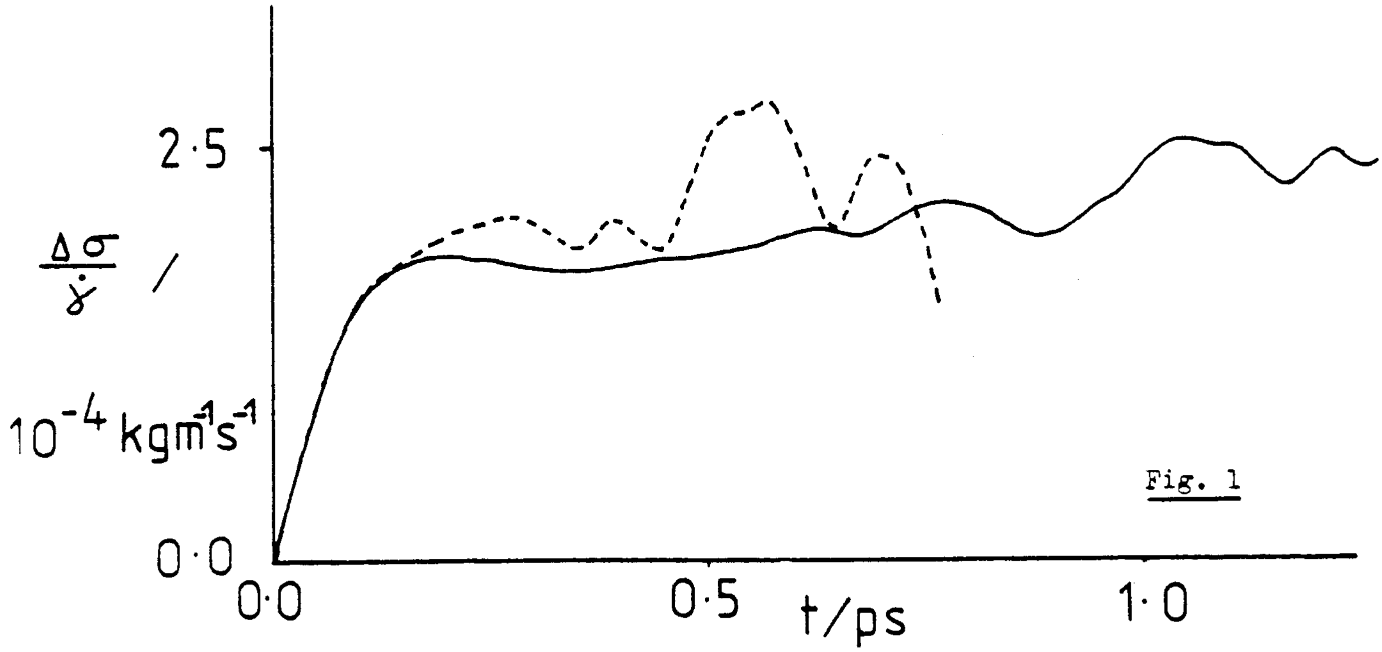


Fig. 1

Fig.1 Shear stress response to a step function perturbation in strain rate γ (------), and the integrated response to a delta function perturbation (———). For diatomic Lennard Jones chlorine, bond length 0.65, $T^* = 1.5$ $\rho^* = 0.49$. Averaged over 7 and 6 segments respectively.

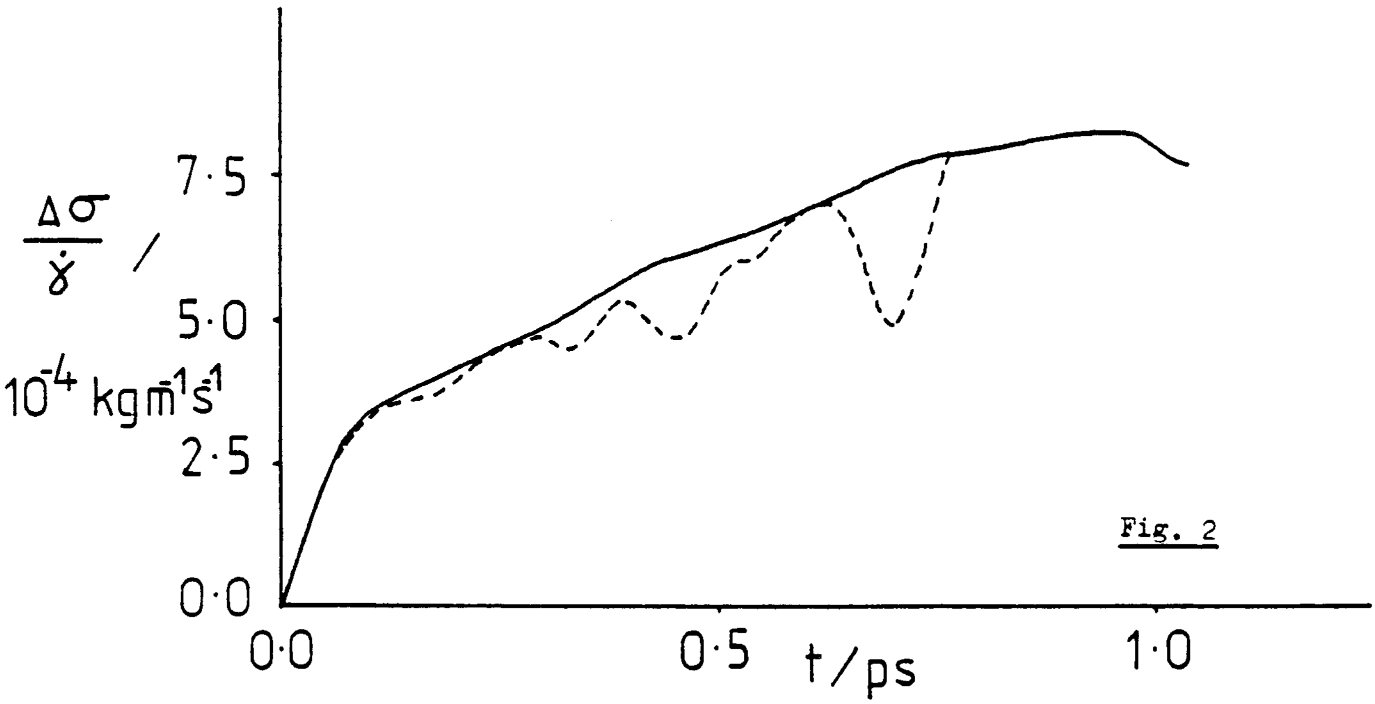
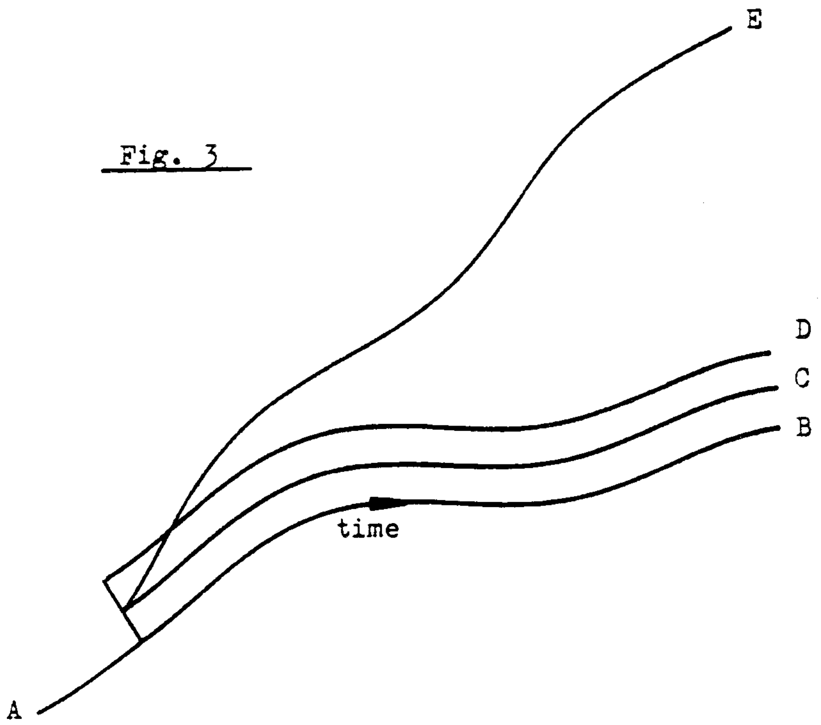


Fig. 2

Fig.2 As Fig.1, $T^* = 0.75$, $\rho^* = 0.59$. Averaged over 8 segments.

If we represent the trajectory in phase space as a line(Fig 3, AB) then a delta function results in an almost parallel path AC. In the linear response regime, a delta function of twice the magnitude will produce another trajectory AD, again parallel but twice the 'distance' from AB. A step function is equivalent to a series of delta functions and therefore produce a series of configurations AE, which move progressivly further from the original set so that at long times considerably more noise appears in the derived responses for small systems.

Fig. 3



The noiseless result of linear response theory (Eqs 2 and 3) is obtained only in the limit of large systems or by averaging over very many segments.

Reference

(1) G. Ciccotti, G. Jacucci, I.R.McDonald, J. Stat. Phys. 21, 1 .(1979).