The computer study of transport processes under extreme conditions

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The computer study of transport processes under extreme conditions

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Abstract. A method is developed to investigate the behaviour of a liquid under the action of a very high shearing force using computer simulated molecular dynamics. Values for the viscosity are calculated but these require more extensive computation for statistical accuracy. A short calculation is, however, sufficient to establish the nature of the processes involved, and to plot the velocity distribution curve; these graphs are presented.

The method abandons the usual homogeneous isotropic cyclic conditions used so far in calculation of transport coefficients, and can be applied to arbitrarily large shear.

1. Introduction

In recent years the use of the molecular dynamics method of computer simulation has extended to the investigation of transport properties of simple fluids. A major study of the hard sphere system has been made by Alder *et al* (1970). The analysis is based on the fluctuation dissipation theory, as described by Helfand (1960).

The consideration of various correlation functions offers a rigorous approach to the evaluation of transport coefficients provided one is close to thermal equilibrium. (It should, however, be stated that any study of transport phenomena is extremely demanding in terms of machine time.) However if one is far from equilibrium the correlation function approach is inapplicable, as are purely analytic approaches. Since the conventional approach is based on quasi-equilibrium considerations, it cannot reveal the time dependent properties or the behaviour of a system under really extreme conditions. Such a situation is not only of academic interest: fluid in a shock wavefront may undergo really extreme conditions for example. It is therefore desirable to examine extreme examples of transport process, both in their own right, and to define the limits of validity of existing theory.

The success of molecular dynamics calculations over the past few years in the prediction of the equilibrium behaviour of a macroscopic system from that of a small model has been considerable. This success is largely due to the fact that a macroscopic piece of material may be represented by a small sample which is considered as being surrounded in all three directions by periodic images of itself. Ensemble averages are obtained by taking several hundred time steps in the integration of the equations of motion of the

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particles. A similar situation can be set up for some nonequilibrium situations and the following section describes a model appropriate to high momentum flux situation.

The use of exact correlation function expressions to obtain, say, the viscosity in the limit of small shear, although exact, is nevertheless indirect; that is the fluid is studied in true equilibrium and from the correlation functions found the effect of a small shear is deduced. In this paper we attempt to simulate the actual sheared motion directly and hence get the momentum transfer exactly. A viscosity coefficient need not exist in these circumstances—indeed hydrodynamics need not exist. The calculation of the computer simulates the actual physical situation and what happens is observed directly, whether or not any simple analytic picture, as in hydrodynamics, exists. This paper is very much a first attempt, and the results rather limited because of the computer power available is limited as compared with the amount required for fully significant results. Nevertheless we feel this approach allows the method to do things outside the range of any analytic treatment and points a new direction in the application of computers to molecular systems.

2. The model

Momentum transport is taken as an example of nonequilibrium phenomena since there is a simple mechanical concept of the process. In simulating a liquid under a high shear stress (and therefore a high momentum flux) the main requisite of any approach is the representation of a macroscopic element of the fluid by a small sample. The box containing the particles is considered as being embedded in a fluid which has a constant velocity gradient in the x direction, say. The cyclic boundary conditions which are normally associated with equilibrium calculations need to be modified to maintain the system under a shearing stress in a steady state. It should be emphasized that the maintenance of a steady state is the basic problem in work of this type; once stationary conditions have been obtained, results of the required accuracy may be produced by taking all averages over a sufficiently large number of time steps in the integration.

The scheme used is shown in figure 1. The box under consideration is surrounded by

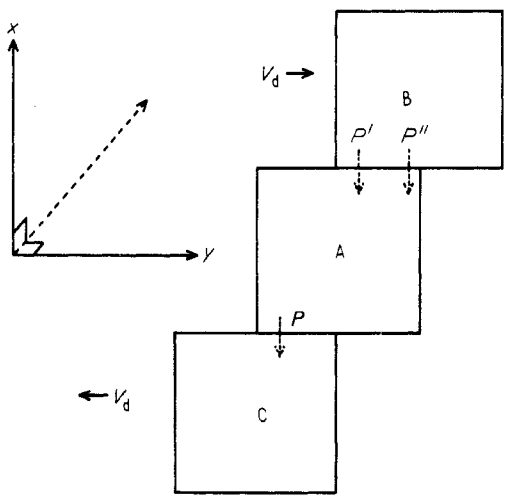

Figure 1.

cyclic images of itself in the yz plane, as in the 'conventional' calculations. The neighbouring cells in the x direction are made to drift with a specified speed V_d in the y direction with respect to the central cell.

The system may be started from a perfect lattice configuration with the neighbouring boxes B and C aligned to A, as in an equilibrium study. The particles in A are given a random velocity whose root mean square value is V_T, the mean thermal speed. In addition to this an atom at the point (X, Y, Z) is given an extra velocity in the y direction ΔV where

$$\Delta V = V_d\left(\frac{X}{L} - \frac{1}{2}\right),$$

resulting in a linear velocity profile centred about the midpoint of box A. This method may be used to initiate the system in as near as possible static conditions. Alternatively, the system may be started in some other state and the decay to static conditions may be observed qualitatively (statistics in such a study are inadequate to form any quantitive conclusions).

Imagine that at some point in the calculation a particle leaves the principal box A at some point P with a y direction velocity component V_y. Under normal cyclic boundary conditions the particle will be reintroduced into the cell at P' with all three velocity components unaltered. If the cell is considered to be an element of fluid, all of which has a linear velocity profile it will be seen that the particle returns to the box at P'' with velocity V' where

$$V'_y = V_y + V_d \tag{1a}$$

$$V'_x = V_x \tag{1b}$$

$$V'_z = V_z \tag{1c}$$

The sign in equation 1a is reversed for particles going through the boundary in the opposite direction.

The method initially employed used the boundary conditions on velocities as shown in (1), but reintroduced the particle at point P', since it was argued that the precise location of re-entry was unimportant. This method, however, fails to produce stable velocity gradients over long periods.

The reason for this failure is attributed to the flux of momentum through the interatomic potential field. In addition to the momentum carried across the walls of the basic cell by a particle, there is another flux Δ_F given by

$$\Delta_F = \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \int_t^{t+\Delta t} \sum{}' F_{ij}(t')\, dt', \tag{2}$$

where Σ' denotes summation over all i and j atoms such that the line joining them crosses

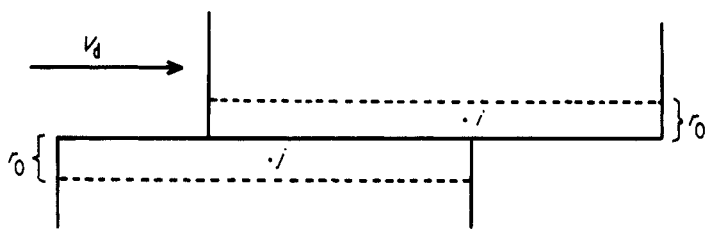

Figure 2.

the boundary of the cell which lies in the yz plane as shown in figure 2 (r_0 is the potential cut-off radius).

The time variation of the quantity

$$F = \sum F_{ij}(t) \tag{3}$$

clearly depends on the shear rate. In the equilibrium case the limiting value of the time average must be zero. To evaluate the contribution in the general case, the force evaluation routine must be modified to allow neighbouring cells to slip past one another. Consider, for example, the interaction of atoms i and j as shown in figure 3. Under

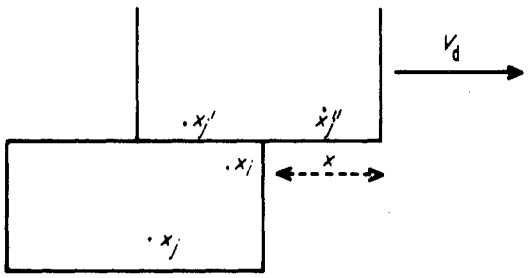

Figure 3.

normal conditions atom i would be considered as interacting with the cyclic reflection of j at position j'. However, since neighbouring boxes are considered as slipping with respect to each other, i is now regarded as interacting with j'' where the displacement $j' - j''$ is in the x direction only having magnitude

$$X = n_t V_d \Delta t - [n_t V_d \Delta t / L] L, \tag{4}$$

where n_t denotes the number of time steps, and $[Y]$ represents the highest integer which is less than Y.

Having modified the calculation of the forces in this way, it becomes important to reintroduce a boundary traversing atom at the appropriate place, that is point P'' of figure 1. This makes the model completely consistent. Any inconsistency in the model would result in nonconservation of energy.

The model as described so far would give rise to a slow heating up of the system. This effect may readily be assessed as follows. In figure 2 the atoms i exert a mean force Δ_F on the atom j, so that

$$\text{mean rate of work} = \Delta_F \bar{V}_X,$$

$\bar{V}_X$ representing the mean relative velocity of i and j atoms,

$$\bar{V}_X = \frac{V_D r_0}{L}$$

where V_D is the speed differential between opposite sides of the box (L). If there are n particles in the model, this work is dissipated among $2nr_0/L$ atoms. Therefore

$$\frac{dT}{dt} = \frac{\Delta_F V_D}{2n\kappa} \tag{5}$$

where κ is the Boltzmann constant. Taking the case for which V_D is one thermal speed,

this expression gives the heating rate of about 8 K per thousand steps (1 step = $2{\cdot}0 \times 10^{-14}$ s). Indeed a trend of this magnitude was observed.

This effect may be compensated by modifying the speeds of particles crossing the y and z boundaries of the box. However, since the present calculations are intended only to establish the validity of the method, the effect was ignored.

3. Results and discussion

In the initial attempts at the calculation, the interatomic forces were evaluated using the method described by Verlet (1967). In this approach, a record is kept of the particles which influence the motion of a given atom. It was found that, using this technique, the energy of the system suddenly increased after several hundred cycles. The explanation of this phenomenon was never firmly established, but no difficulties were encountered when the forces were evaluated directly. It is possible, therefore, that velocity correlations are jeopardizing the rapid method of evaluating the forces. The direct enumeration of the forces at each time interval increases the machine time by a factor of three. In the calculations the initial 350 steps were calculated using the rapid technique and from there on all forces were calculated explicitly.

Three runs of the program were made, all at a density of 1·41 g cm^{-3} and a temperature of 85 K using liquid argon. The first run considered a shear across the box such that the opposite boundaries had mean speeds differing by one thermal velocity. At this rate of shear the mean velocity gradient was remarkably stable. For the purposes of evaluating the gradient, the unit cell was divided into an upper and lower half since smaller subdivisions would not be statistically adequate. The program did, nevertheless, monitor the velocity profile in ten equal portions of the cell, although this was merely to provide qualitative information. Taking the unit speed as being defined by the hard core repulsion term, the mean velocity at 85 K is 0·84 which would imply that the total momentum in the lower portion of the box should oscillate about 52·5, whilst that in the upper portion would oscillate in antiphase to it. It is found that in calculating the velocity profiles over 500 time steps the means of the velocity in the two portions of the box were $-52 \pm 1{\cdot}4$ and $55 \pm 1{\cdot}2$. It will be seen that the convergence of this quantity is good. The variation in time is shown in figure 4.

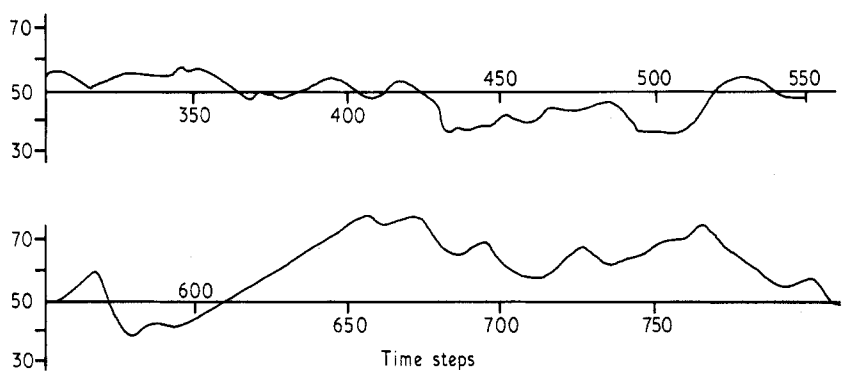

Figure 4. Variation of ΣV_i in the upper half of the box.

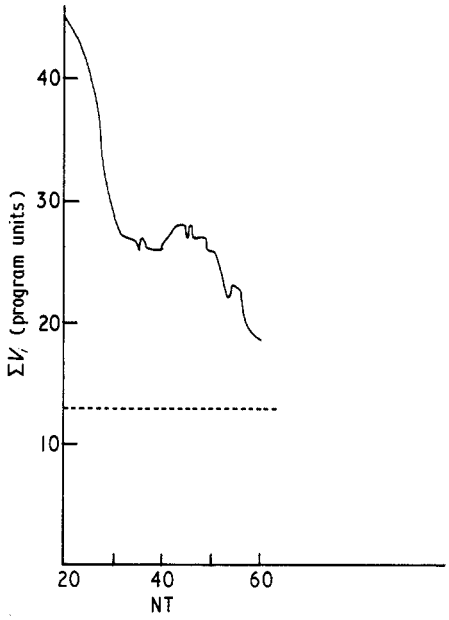

Figure 5. Decay of $\sum V_i$.

In considering figure 4 it should be noted that the fluctuations about the mean value are the background noise of the model rather than a fixed percentage error about the mean gradient. This implies that as the gradient decreases, statistically meaningful results become progressively more difficult to obtain.

Representing the thermal speed by V_T the three runs made were performed with values for the velocity differential across the box of V_T, $V_T/4$ and $V_T/10$. The first of these runs was initiated with the system having a higher velocity gradient than the boundary conditions would maintain. The decay of the gradient in this case towards its stable value in the initial stages of the calculation is shown in figure 5. In all three runs the rate of particle transmission was monitored and this showed no significant dependence on the velocity gradient. In the case of the highest gradient the velocity distribution curve of the system

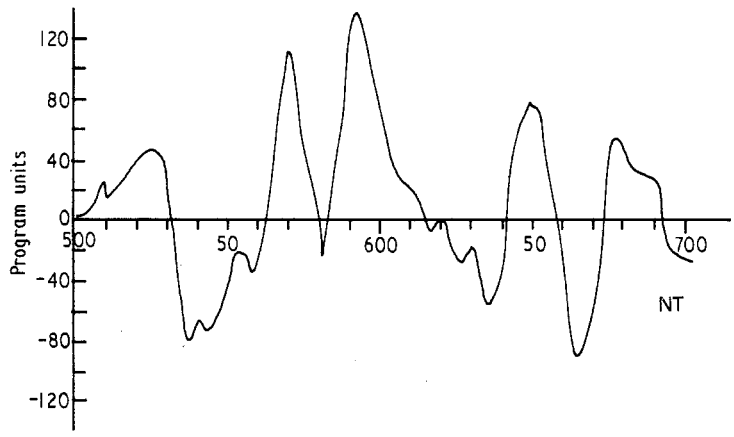

Figure 6. Variation of Δ_F.

was calculated over 500 time steps. Figure 7 shows the distribution of the y component of molecular velocities about the local mean, that is

$$f\left(V_y - \frac{V_d X}{L}\right)$$

for the entire box. Figure 7 shows the same distribution when only the top half of the box

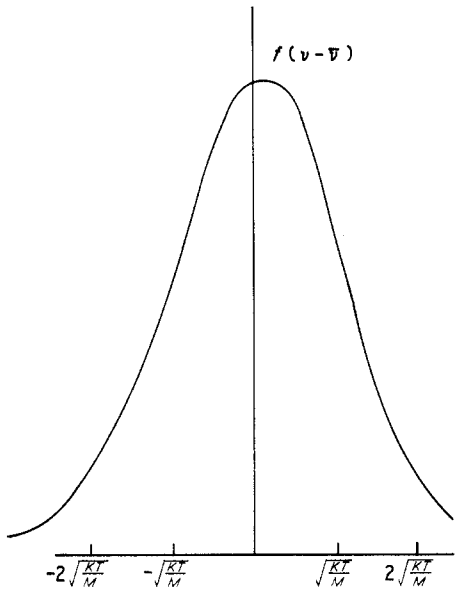

Figure 7. Velocity profile.

is taken into consideration. It will be seen that although these curves exhibit some deviations from gaussian behaviour, these deviations are remarkably small.

The experiments made with the velocity differential of $V_T/4$ were applied to a closer study of the transport mechanism. The flux of momentum through the interatomic field was monitored throughout the whole calculation (700 time steps). It was found that this momentum flux was very much a random function and it is this fact which makes the computation of transport phenomena difficult. The graph of this function is shown in figure 6 over the time interval which was used for the averaging process. Since the calculation of this case was again started from a nonstatic situation the first 500 steps in the integration were ignored and the averages were taken over the time steps 500 to 700. Let

$\dot{n}$ = rate of particle flux

V_d = speed differential,

h be the time increment, and

Δ_F be defined by equation 2,

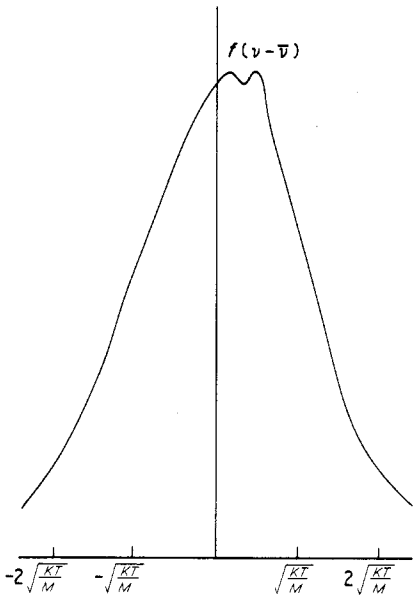

Figure 8. Velocity profile.

then

$$P_{ij} = \eta \frac{\partial V_i}{\partial x_j},$$

$$P_{ij} = \frac{\Delta_F h + \dot{n} V_d}{L^2} \tag{6}$$

$$\frac{\partial V_i}{\partial X_j} = \frac{V_d}{L}$$

and then finally

$$\eta = \frac{\Delta_F h}{L V_d} + \frac{\dot{n}}{L}. \tag{7}$$

The calculation revealed that at this gradient about 85% of the momentum flux is due to the field interactions. The final value for the viscosity coefficient is 5·2 millipoise, although the statistical uncertainty in this figure is very large. This may be compared with the experimental quasi-equilibrium value of 1·75 millipoise at the same temperature and density. The accuracy of the current results is not sufficient to draw the firm conclusion that the transport coefficient increases with velocity gradient. It is significant, however, that such a short run of the program yields answers which are of the correct order of magnitude and this gives rise to the hope that the method could be used to obtain numerically meaningful results, given a calculation of, perhaps, 20000 time steps.

The statistical convergence of the method may be improved in several ways. The calculation of momentum transport across the boundary of the box was described and, as has been remarked, it is this function which causes the statistical difficulties in the calculation. In calculating this momentum flux it is possible to take any yz plane as the reference. Obviously, it is pointless in calculating the flux through planes which are too

close together but it would be valid to take, say, 4 reference planes equally spaced along the length of the box in the x direction. Further improvements in the averaging process could be achieved by considering a set of initial conditions, in much the same way as is done in the conventional approach. Nevertheless it is felt that the foundations of a general method have been developed and the qualitative results obtained warrant further development.

4. Concluding remarks

In this paper a class of problems not hitherto considered in molecular dynamics have been approached. The usual methods of considering transport phenomena, as described in the first section, cannot be applied to the study of materials under extreme conditions. The consideration of such a situation is not only of academic interest. A process such as has been described in the calculations may occur in practice (in a shock wave for instance). It is therefore of both practical and theoretical importance to study the breakdown of hydrodynamic behaviour.

To the best of the authors' knowledge, this is the first time that noncyclic boundary conditions have been applied. It would seem that a similar modification of boundary conditions could be applied to study the dynamics of a situation in the region of a density gradient. The third transport process, namely the transport of energy, is somewhat more complex since we have no simple mechanical picture on which to base the calculations.

Acknowledgments

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