

Tail Shortening by Discrete Hydrodynamics

J. Kiefer¹ and P. B. Visscher¹

Received May 12, 1981

A discrete formulation of hydrodynamics was recently introduced, whose most important feature is that it is exactly renormalizable. Previous numerical work has found that it provides a more efficient and rapidly convergent method for calculating transport coefficients than the usual Green-Kubo method. The latter's convergence difficulties are due to the well-known "long-time tail" of the time correlation function which must be integrated over time. The purpose of the present paper is to present additional evidence that these difficulties are really absent in the discrete equation of motion approach. The "memory" terms in the equation of motion are calculated accurately, and shown to decay much more rapidly with time than the equilibrium time correlations do.

KEY WORDS: Molecular dynamics; transport coefficients; viscosity; time correlation functions; long-time tails.

1. INTRODUCTION

In this paper we report numerical results for soft-sphere equations of motion in a recently introduced exactly renormalizable discrete formulation of hydrodynamics.⁽¹⁾ We begin by reviewing the reasons for expecting such a formulation to be useful. Renormalization methods may be applied whenever one wishes to describe a system on several different length (and in our case also time) scales.^(3,4) Typically one knows the laws governing the system on a microscopic scale (the interatomic potential in a fluid, or the spin Hamiltonian in a magnetic lattice) and wishes to predict the results of an experiment on a macroscopic scale (say a viscosity measurement in the fluid, or a susceptibility measurement in the magnet). The large-scale behavior can be calculated directly and accurately only in trivial model systems. However, in magnetic systems it has been found useful to increase the length scale in stages: combine several spins (8, in a simple cubic

¹ Department of Physics and Astronomy, The University of Alabama, University, Alabama 35486.

lattice) into one “block spin” and set up a new coarse-scale spin Hamiltonian describing the behavior of the block spins. If the Hamiltonian is parametrized in terms of a set of Hamiltonian parameters, the coarse-scale parameters can sometimes be computed by a mathematical procedure from the original (fine-scale) parameters. Such a Hamiltonian is said to be renormalizable, and the procedure is called a renormalization transformation. The properties of the system on an arbitrarily large (i.e., macroscopic) scale can be obtained by performing this transformation repeatedly. These renormalization transformations have proved to be enormously useful in predicting macroscopic behavior near critical points (critical exponents, etc.). Other methods, such as series expansions of correlation functions via graphical perturbation methods, are very singular and suffer severe convergence problems^(5,6) due to the long spatial range of the correlations near a critical point.

A noncritical fluid is a very different physical system from a critical magnetic lattice, but the basic problem of deducing macroscopic behavior from microscopic laws is the same. A further similarity is that series expansions (in the density) obtained from graphical perturbation theories are singular in fluids.⁽⁷⁾ The singularities in this case do not reflect spatially long ranged equal-time correlations, but long ranged two-time correlations (the “long-time-tails”).⁽⁸⁾ Direct calculations of time correlation functions (such as those required in Green–Kubo^(9,10) calculations of transport coefficients) have severe convergence problems as a result of these tails.

It would appear, therefore, that a renormalizable theory of fluids would be of interest: one should look for a description of a fluid on a particular distance scale W , i.e., a discrete description, and a way of transforming it into a description on a scale $2W$. Since fluids are usually described by equations of motion rather than Hamiltonians (Hamiltonian descriptions of dissipative systems being very awkward), we should look for an equation of motion describing the system on our distance scale W . Since some of the singularities we wish to avoid are associated with long-time correlations, we should also be able to coarsen the time scale. This can be done if the description is discrete in time; let us denote the time scale associated with a particular equation of motion by τ . Such a renormalizable discrete theory has been developed by one of us,^(1,2) and is sketched in the next section.

2. DISCRETE HYDRODYNAMICS: A RENORMALIZABLE FORMULATION

We would like to find a renormalizable discrete analog of the continuum Navier–Stokes equations of motion. It should specify how some

discrete analogs of the continuum hydrodynamic variables change with time. The continuum densities of the five conserved hydrodynamic quantities (particle number, energy, and momentum, labeled below N , E , P_x , P_y , and P_z) have obvious discrete analogs, given our desired length and time scales W and τ . These analogs are the contents of the conserved quantities in cubical cells of width W , at times $m\tau$ ($m = \text{integer}$). We shall denote the content of the quantity labeled α ($\alpha = N, E, P_x, P_y, \text{ or } P_z$) in a cell labeled l by $c(\alpha, l, m)$. The continuum equations predict fluxes; the discrete analog of a flux is evidently a transfer: the amount of a quantity α ($= N, E, \text{ or } P$) transferred across a square face (labeled f) during the time interval $[m\tau, (m+1)\tau]$. We shall label this interval by its midpoint $m + 1/2$. The transfer will be denoted $x(\alpha, f, m + 1/2)$.

What do we mean by “predicting” the transfer $x(\alpha, f, 1/2)$, over the time interval $[0, \tau]$, from information about the previous state of the system? The maximum amount of such information we could have at time 0 would be the contents $c(\alpha, l, 0)$ at time 0 and the previous transfers $x(\alpha, f, m < 0)$ (note that the previous contents are completely determined by these data.) These “history variables” at times $m \leq 0$ do not determine the future transfers uniquely, of course. But we expect them to determine some sort of average values for the transfers. This can be made precise by defining, for each set of values for the history variables, the ensemble of systems having exactly these values. The ensemble distribution function is taken to be uniform within the phase space satisfying this criterion; it is written down explicitly in Ref. 1.

The best prediction for the transfer $x(\alpha, f, 1/2)$ is then its mean value in this ensemble, which we shall denote by $[x(\alpha, f, 1/2)]$. The mean $[x]$ is a function of the assumed values of the history variables h ; this function is the discrete analog of the continuum equation of motion. However, this function does not determine the system’s dynamics uniquely, since it contains no information on fluctuations and correlations among the transfers. More importantly, it is not renormalizable, i.e., it does not determine the corresponding function for cells of width $2W$. Renormalizability requires complete information on the probability distribution of the transfers; in principle this is contained in the set of all moments of the transfers (all means of products). Therefore we define the “discrete equation of motion” to be this set of moments, each of them a function of all history variables (contents at time 0 and earlier transfers).

For purposes of numerical calculation, we shall parametrize this equation of motion. In linear hydrodynamic systems we expect the fluxes to be proportional to density gradients; in our discrete analog the transfers should be proportional to content differences. We may exploit this expectation with no loss of generality by expanding the flux moments in power

series in their arguments, the history variables. Then the expansion of the mean $[x(\alpha, f, 1/2)]$ has the form

$$[x] = \sum_h B_{x;h} h + \dots \quad (2.1)$$

where the power-series coefficient $B_{x;h}$ describes the influence on the transfer x of the history variable h (a content or previous transfer; the sum ranges over all α , all cells, and all times). We have eliminated constant terms in the expansion by replacing the transfers and contents by their deviations from their equilibrium values. Some of the nonlinear coefficients denoted by \dots in Eq. (2.1) have been included in previous calculations⁽¹¹⁾ and found to change the results by only one or two percent; for simplicity we will omit them here. Higher moments of the transfers have expansions similar to Eq. (2.1).⁽²⁾ We will refer to the totality of all coefficients in Eq. (2.1) and these higher equations as the equation of motion parameters ("the B 's"). Though the above procedure formally defines $B_{x;h}$ uniquely, it is not easy to make rigorous, since the functions we expand in power series are highly singular.^(1,2) We believe, however, that $B_{x;h}$ can be uniquely defined in terms of moments [see Eq. (2.2) below].

We now argue that the discrete equation of motion is exactly renormalizable. In a well-behaved system the discrete equation of motion uniquely determines the equilibrium correlations of the discrete variables (a more careful discussion of this point is to be found in Ref. 1). These correlations trivially determine the correlations of the coarse-scale variables (contents and transfers for cells of width $2W$, which are just sums of the fine-scale variables). These in turn determine⁽¹⁾ the coarse-scale equation of motion. The result is that the discrete equation of motion is *exactly renormalizable* in space, and the same reasoning shows it to be exactly renormalizable in time as well.

This renormalizability means that in principle the equation of motion parameters B for cell size W and time interval τ exactly determine those for cells of size $2W$ and/or time 2τ . An explicit coarsening procedure for computing them has been given.^(2,12) Fixed points under coarsening transformations have been found numerically for simple dissipative systems⁽¹²⁾ which are analogous to the fixed points studied in critical phenomena; in fact the fixed points of a simple critical system (the Gaussian model) have also been computed.⁽¹³⁾

In the present paper, however, we are interested in the calculation of transport coefficients in fluids, from molecular force laws. A renormalizable formulation of hydrodynamics allows us to do this by a three-stage process: (1) the molecular laws can be related to microscopic-cell discrete equations of motion (EOMs), (2) these can be transformed into macroscopic-cell

discrete EOMs, (3) which can in turn be used to determine transport coefficients. Step (1), the computation of the microscopic discrete EOM parameters $B_{x;h}$ [Eq. (2.1)] can be accomplished by molecular dynamics simulation, using a procedure described in detail in Ref. 17. This is done by computing equilibrium averages (denoted by $\langle \rangle$) of products of discrete variables. An equation from which $B_{x;h}$ can then be calculated is obtained by multiplying Eq. (2.1) by the history variable h' and averaging it over the equilibrium ensemble:

$$\langle xh' \rangle = \sum_h B_{x;h} \langle hh' \rangle \quad (2.2)$$

Methods for the solution of Eq. (2.2) are described in detail in Section 3. Step (3), the calculation of transport coefficients, is easy to do in the large-cell limit. We need only apply the equation of motion to a uniform-gradient system and look at the resulting flux [see Eq. (4.1)]. In the large cell limit, fluctuations are negligible (relative to mean values) and this can be done unambiguously. One does not expect to need enormously large cells to get essentially the macroscopic transport coefficients; these should become independent of cell size W very rapidly as one doubles W . In fact, it appears from previous numerical work^(11,14) that the W we have used in step (1) gives a good approximation, i.e., step (2) has little effect on the outcome. We shall therefore defer the numerical renormalization procedure to a later paper, and concentrate here on step (1).

As mentioned in Section 1, the motivation for our approach was that the renormalization technique might allow us to avoid the serious convergence problems of the Green–Kubo method, which arise from the long-time tail of time correlation functions. It is important to determine whether we have indeed avoided them, or whether they are going to appear in some other form. Since the tails are not important at macroscopic times, such problems are most likely to appear in the small-cell EOM parameters $B_{x;h}$. Among these are parameters $B_{x;x}$, which describe the dependence of $x(\alpha, f, 1/2)$ on a previous transfer $x(\alpha', f', m' < 0)$. If these “memory” parameters have a long-time (large $|m'|$) tail like the time correlation functions, we are in trouble. One can argue theoretically that they should not.⁽¹⁵⁾ The equilibrium correlation $\langle xx' \rangle$ between two transfers (or fluxes) can be thought of as measuring how much information the knowledge of x' gives about x ; this can be substantial even if the transfers are widely separated in time because they may both be part of a large-scale eddy fluctuation. The parameter $B_{x;x'}$, on the other hand, measures how much additional information x' (at a time $m'\tau < 0$) provides about x (at time $\tau/2$), when the variables at all intervening times are fixed and known. In other words, $B_{x;x'}$ describes a highly constrained ensemble in which large-

scale eddy fluctuations are frozen; we do not expect to see the long-time tail effects. However, previous numerical results have not been accurate enough to verify this unambiguously. It is the principal purpose of this paper to present numerical proof of this (see Section 5). We begin, in the next section, by describing the calculation of the equation-of-motion parameters.

3. CALCULATION OF EQUATION-OF-MOTION COEFFICIENTS

Equations (2.2) involve an infinite number of equation-of-motion coefficients $B_{x;h}$. We must somehow choose² a finite subset of these, which we shall call BLIST, to include in the calculation. Equations (2.2) contain an equation for each $B_{x;h}$ in BLIST, with left-hand side $\langle xh' \rangle$ and many terms involving other B 's in BLIST and various averages $\langle hh' \rangle$ on the right-hand side. Though the number of such terms is finite, it is very large, and many of the terms are numerically negligible. Since the computation of $\langle hh' \rangle$ from molecular dynamics data is quite time-consuming, we shall use only the most important terms on the right-hand side.

In choosing BLIST we must be guided by our intuitive expectation that the transfer x will be most influenced by history variables h which are nearby in space and time, and that the influence will generally decrease with distance. This assumption may then be justified *a posteriori* by the numerical results. Thus a $B_{x;h}$ which is important is assumed to have some neighbor (in space or time) which is more important. This suggests an iterative algorithm for choosing BLIST which works its way out through less and less important $B_{x;h}$ by enumerating the neighbors of h 's already included. Such an algorithm must begin with a small "startup" BLIST, which contains enough $B_{x;h}$'s so all others can be reached by chains of neighbors.

A specific algorithm for solving Eq. (2.2) by enlarging BLIST was described in Ref. 11. It was a term-oriented algorithm, in the sense that TLIST, a list of terms $B_{x;h}\langle hh' \rangle$ appearing on the right-hand side of Eq. (2.2), was kept, along with BLIST and a list of averages AVLIST. When BLIST was enlarged by adding neighbors of $B_{x;h}$, TLIST and AVLIST were also enlarged in a prescribed way. This scheme has several disadvantages: (1) The list of terms is very long, and enumerating all the neighbors of several hundred terms by hand is a tedious and error-prone procedure, and (2) the matrix coupling the B 's in Eq. (2.2) (essentially the covariance matrix of the

² The problem of choosing which B 's are most significant has often been addressed in the literature of linear regression theory. The present problem differs from most of this work in that the number of h 's is infinite. The possibility of leaving out terms is not usually considered. Our procedure has some resemblance to the method called "forward regression"; see for example Ref. 16.

history variables h) often has very small eigenvalues. This is due to approximate linear dependences among the history variables, a problem common in the literature of linear regression theory⁽¹⁶⁾ and referred to as “multicollinearity.” The result is that apparently small truncation errors in off-diagonal elements of the matrix can push the eigenvalue to zero and make the matrix singular. The symptoms of this phenomenon occur when a new B is added to BLIST: values of other B ’s change by large amounts, and their statistical fluctuations increase suddenly. These problems can be avoided by being very conservative about omitting terms from Eq. (2.2), but this is very difficult when they must be enumerated by hand.

The alternative to a term-oriented algorithm is an average-oriented one, in which only a BLIST and an AVLIST are kept. All terms involving these B ’s and averages are included, and are generated automatically. This is the approach used in the present paper. It requires a much more sophisticated set of programs. Each $B_{x;h}$ (or $\langle hh' \rangle$) may be rotated or translated into other positions by symmetry operations of the cubic group.⁽¹⁷⁾ Only one of these positions should be listed in BLIST (or AVLIST). Thus we require a criterion for determining this unique standard position, and an orienting algorithm for finding the standard position equivalent to any given initial position. Then the equations (2.2) may be generated automatically. For each $B_{x;h}$ in BLIST, we consider in turn each $B_{x;h'}$ from BLIST. A rotation algorithm enumerates all equivalent rotated positions for h' . Each of these determines an average $\langle hh' \rangle$, which must be oriented into its standard position before being looked up in AVLIST.

Once we have such a program for creating and solving Eqs. (2.2) for a given BLIST and AVLIST, we need only find an iterative procedure for expanding these lists. We may begin by enumerating all neighbors of each $B_{x;h}$ in BLIST. If h is a content $c(\alpha, l, m)$, for example, its neighbors are $c(\alpha, l', m)$, where the cell l' is displaced from l by one unit along any axis, or $c(\alpha, l, m - 1)$ which has been displaced in time. This gives us a supplementary list we may call BNBR. We cannot include all these in the new BLIST, since such a procedure would never terminate. To keep BLIST short, we require that a new member be both statistically *significant* and *important*. The latter two notions require definition.

A number of tests of significance exist in the literature of linear regression,⁽¹⁶⁾ most of which involve comparing an estimate of $B_{x;h}$ to an estimate of its variance, $\sigma(B_{x;h})$. The significance ratio $B_{x;h}/\sigma^{1/2}(B_{x;h})$ has roughly a Student t -distribution (which is approximately a Gaussian distribution of variance 1). We have estimated $B_{x;h}$ from its Eq. (2.2) using the B ’s in BLIST on the right-hand side:

$$\langle xh \rangle = B_{x;h} \langle h^2 \rangle + \sum_{B_{x;h'} \in \text{BLIST}} B_{x;h'} \langle h'h \rangle \tag{3.1}$$

We have estimated its variance as the standard deviation of the mean of results from four molecular-dynamics runs. One could then regard $B_{x;h}$ as significant when the significance ratio exceeds (in absolute value) some fixed value, say 1.0. The probability of this occurring spuriously when the correct value of B is zero is (according to the t distribution) about 40%. It is quite likely to occur for at least one of the seven neighbors of a B . Thus this is an unacceptable method, which can add infinite chains of spuriously significant B s. Increasing the required significance ratio to 2.0 or 3.0 is not desirable, since it would lead to loss of much information which probably is significant. We may take advantage of our expectation that the B 's drop off fairly rapidly as one moves away from the startup B 's to construct a compromise criterion: $B_{x;h}$ is significant if (a) $|B_{x;h}/\sigma| > 1$ and (b) this ratio exceeds 2 for either B or some neighbor and (c) this ratio exceeds 3.0 for B , some neighbor, or some neighbor's neighbor, and (d) The series of tests (a),(b),(c),(d), . . . is to be terminated when the set of neighbors involved includes a startup B ; these cannot be expected to have larger neighbors. This criterion prevents long chains of spurious B 's, without ignoring the last in a series of genuinely significant B 's.

The procedure just described for enlarging BLIST will terminate when all statistically significant B 's have been computed. However, often one is primarily interested in some specific function of the B 's, say $F(\{B\})$; F could, for example, be the viscosity. Many of the B 's could be omitted with virtually no effect on F . To identify these, we define the "importance" of $B_{x;h}$, called $\Delta F(B_{x;h})$, as the change in F caused by adding $B_{x;h}$ to the BLIST used in computing F . It may be computed by actually subtracting two values of F , or by a linear approximation (computing the derivative of F with respect to B , and multiplying by the value of B). We may then call B "important" if $\Delta F(B)$ exceeds some tolerance to which we would like to calculate F , say FTOL.

The practical lower limit on FTOL is set by the statistical uncertainty of F ; there is no point trying to lower FTOL (effectively a truncation uncertainty) very far below this. Since the statistical uncertainty is initially unknown, we set FTOL equal to some large value initially, and lower it as BLIST is enlarged.

We have not yet described the procedure for enlarging AVLIST. This is done by defining $\Delta F(\langle hh' \rangle)$ as the change in the final result F due to including the average $\langle hh' \rangle$. Computing $\Delta F(\langle hh' \rangle)$ involves knowledge of all the terms in which this average (or an equivalent one) appears. If $|\Delta F(\langle hh' \rangle)| > S \times \text{FTOL}$ we regard $\langle hh' \rangle$ as important and add all its neighbors to AVLIST. They are then computed from the molecular dynamics data before proceeding. The coefficient S is a safety factor, which we have taken to be 1/4. This causes the algorithm to be very conservative about

omitting averages, to avoid the singularity problems mentioned at the beginning of this section.

We have not yet specified the startup lists BLIST and AVLIST. The simplest choice is to use one B from each equivalence class under the neighbor relation defined above, i.e., essentially one for each pair of α 's. We have done this in the present calculation, and similarly for the averages. Earlier calculations⁽¹¹⁾ used a more complicated notion of "neighbor" which led to a smaller startup BLIST. With an automated program for generating Eqs. (2.2) this is no longer so advantageous; in fact with the old startup BLIST we wasted several iterations getting to the point where we now begin.

A total truncation uncertainty for F can be defined⁽¹¹⁾ as the square root of the sum of the squares of $\Delta F(B)$ for B in BNBR (i.e., not in BLIST). In the present work we have calculated this for several functions $F(\{B\})$; not only the viscosity but each B itself (whose value changes when BLIST is augmented). It is always possible to make the truncation uncertainty considerably less than the statistical uncertainty; when this has been done we give only the statistical uncertainty. However, for relatively unimportant B 's this is not necessary, and we quote the larger truncation uncertainty (see Figs. 1 and 2).

4. NUMERICAL RESULTS

We have calculated the equation-of-motion parameters $B_{x;h}$ for a system of 32 soft spheres, using the algorithm of Section 3 to solve Eq. (2.2). The required cell-variable averages were computed as in Ref. 14, using the molecular dynamics integration algorithm of Verlet,⁽¹⁸⁾ in which coupled first-order Hamilton equations for the particle positions and velocities are integrated numerically. We chose the cell width W so that each cell has an average of four particles. Thus the system has eight such cells, arranged in a cube. We used an integration interval $\Delta t = 0.0099s (M/kT)^{1/2}$; this was sufficiently small that the total energy was conserved to one part in 10^3 . We use the standard dimensionless units for soft spheres⁽¹⁹⁾ (length unit = effective radius s , energy unit = kT , mass unit = particle mass M .) Previous discrete hydrodynamics calculations^(11,14) have used a system with reduced density⁽¹⁹⁾ $\rho_r = 0.6$, at which the viscosity is about 50% higher than that given by the Enskog theory.⁽¹⁹⁾ Good agreement with independent calculations of the viscosity by Ashurst and Hoover⁽¹⁹⁾ was obtained. To provide another test of the discrete technique, we have used a higher density $\rho_r = 0.8$. This is almost the freezing density ($\rho_r = 0.813$).⁽¹⁹⁾ In fact the 32-particle system shows a tendency to freeze even at $\rho_r = 0.8$, because of periodic boundary effects. The nucleation rate

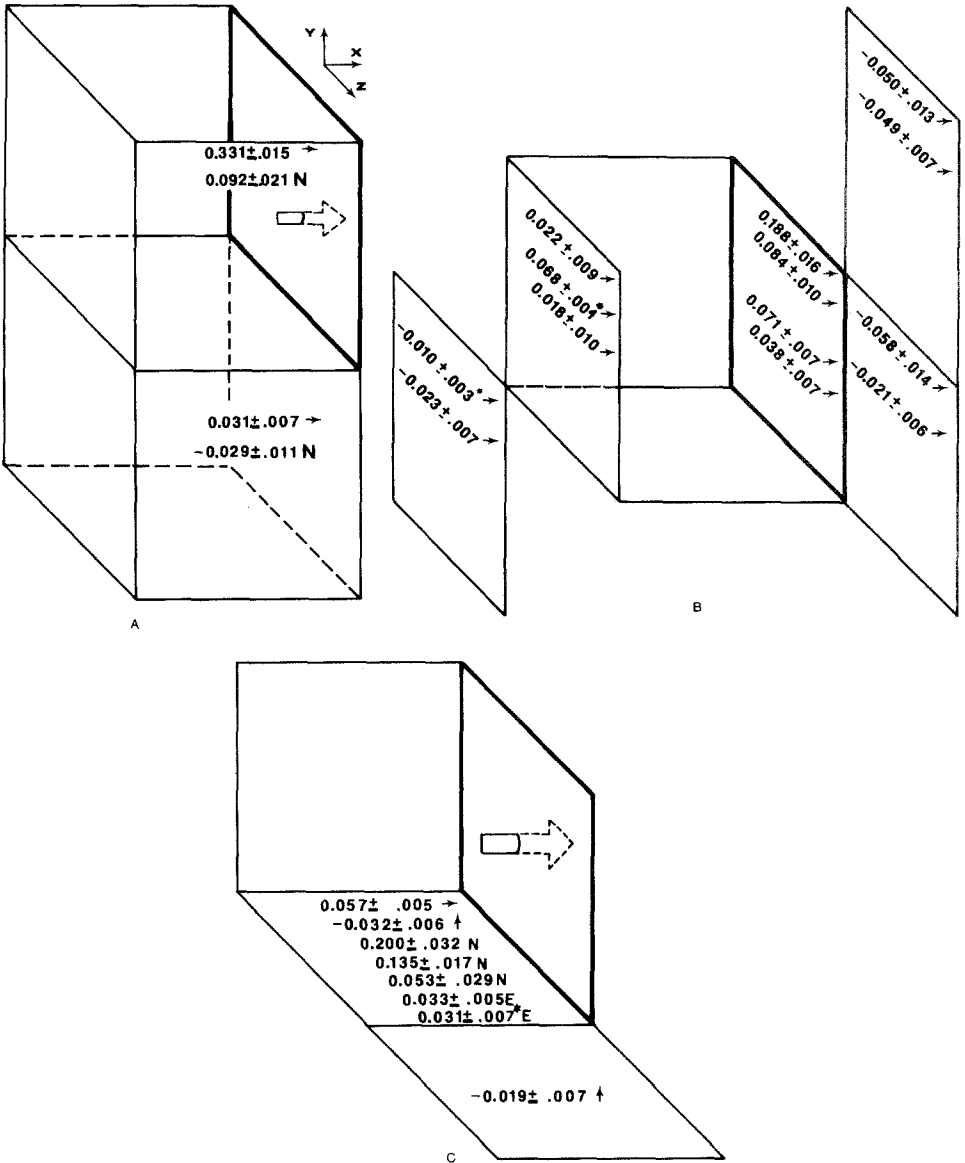


Fig. 1. Longitudinal momentum transfer equation-of-motion parameters $B_{x,h}$, for x = transfer of longitudinal momentum (P_x) across the face outlined with heavy lines. For each content or transfer h , $B_{x,h}$ is written in the cell or face where h is located. For clarity, only the contents $h = c(\alpha, l, 0)$ are used in (a), in the format $B_{x,h} \pm$ statistical uncertainty (or truncation uncertainty if it is larger; this is indicated by an asterisk). The right-most symbol is α , i.e., E, N, or an arrow indicating a momentum direction. The effects of previous x -transfers $h = x(\alpha, f, -1/2)$ are given in (b) in the same format, with $x(\alpha, f, -3/2)$, $x(\alpha, f, -5/2)$ directly below. [When $x(\alpha, f, -1/2)$ or $x(\alpha, f, -3/2)$ is not in BLIST, its place is held by asterisks: ***.] Part (c) gives the effects of y transfers.

is low enough, however, that a solid formed only three times during our simulation of $18,000\Delta t$. Each time, we backed up to a time before nucleation began and perturbed the trajectories slightly, by integrating for 400 steps of length $\Delta t/2$, and then continued with steps of length Δt . This was sufficient to prevent the nucleation, and provided a simulation of a metastable liquid.

The data were analyzed by computing cell contents and transfers for cells of width $W = 1.523$, with transfer time $\tau = 0.1981$ (i.e., $20\Delta t$).

We have calculated $B_{x;h}$ for two types of transfer: longitudinal momentum and shear momentum. The numerical results are presented in Figs. 1 and 2, respectively. The numbers there are the $B_{x;h}$'s in BLIST. In the longitudinal case, we regarded each B in BLIST as one of the desired final results (F in the algorithm of Section 3) determining importances of B 's and averages; this causes the algorithm to try to minimize truncation errors of the most important B 's. In the shear case, we are ultimately interested in calculating the viscosity η :

$$\eta = M\rho \frac{W^2}{\tau} \sum_l B_{x(P_y, f, 1/2); c(P_y, l, 0)} (l - f)_x + \eta \sum_{m=-\infty}^{-1/2} \sum_{f'} B_{x(P_y, f, 1/2); x(P_y, f', m)} \quad (4.1)$$

The faces f and f' are normal to the x direction. Equation (4.1) is derived in Ref. 15 by considering a system with a uniform velocity gradient; η is the ratio between the mean transfer of shear momentum [$[x(P_y, f, 1/2)]$, from Eq. (2.1)] and the velocity gradient. We have omitted here some numerically small terms. We have used η as F in our calculation of the shear transfers, so the algorithm tried to minimize the truncation uncertainty of η . Unfortunately, it turned out that the value chosen for τ was too large to provide a realistic estimate of η in a $2 \times 2 \times 2$ system of cells. In such a small system, only the effects of momentum contents of cells actually touching the plane of the transfer x can be computed⁽¹⁷⁾ (see Fig. 2). If momentum travels across the face from further away, this information is lost because of the periodic boundary conditions, leading to an underestimate of the viscosity. The same problem occurred in a previous viscosity calculation at the lower density $\rho_r = 0.6$;⁽¹⁴⁾ it is solvable by using a smaller τ , which we intend to do. There are several indications that this is happening: (i) The influence of the cell at the upper right in Fig. 2a, which touches the face of the predicted transfer only along an edge, is as large as that of the lower right cell, which touches the face everywhere. This suggests that the momentum can move quite far during τ . (ii) The fraction of the P_y content of a column of cells (in a $2 \times 2 \times 2$ system, just the two cells just mentioned) which leaves it in time τ is four times the sum of these

two $B_{x;c}$'s, or about 0.83. It was argued in Ref. 14 that this suggests that shear momentum probably travels across more than one cell. (iii) The actual viscosity estimate [Eq. (4.1)] implied by Fig. 2 is about 3.2, compared to Ashurst and Hoover's $\eta = 5.4 \pm 0.5$.⁽¹⁹⁾

It is known^(12,15) that transport coefficients are very sensitive to small changes in $B_{x;c}$ for distant cell contents c , and may therefore have large errors in a finite-system simulation even when the nearby $B_{x;c}$'s have essentially their infinite-system values. So this difficulty in calculating η should not deter us from taking seriously the general behavior of the equations of motion.

It can be seen from Figs. 1 and 2 that the results are now accurate enough to give a good general picture of the discrete equations of motion, at least for a periodic system. Our original expectation, that the influences of history variables decrease as they get farther in space or time from the predicted transfer, is confirmed. It is noteworthy that while the total effect

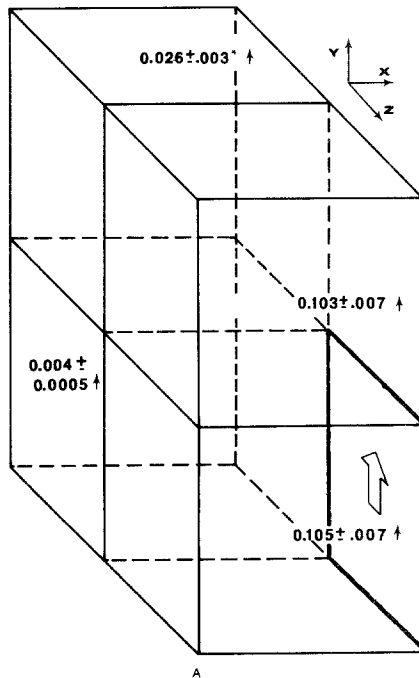
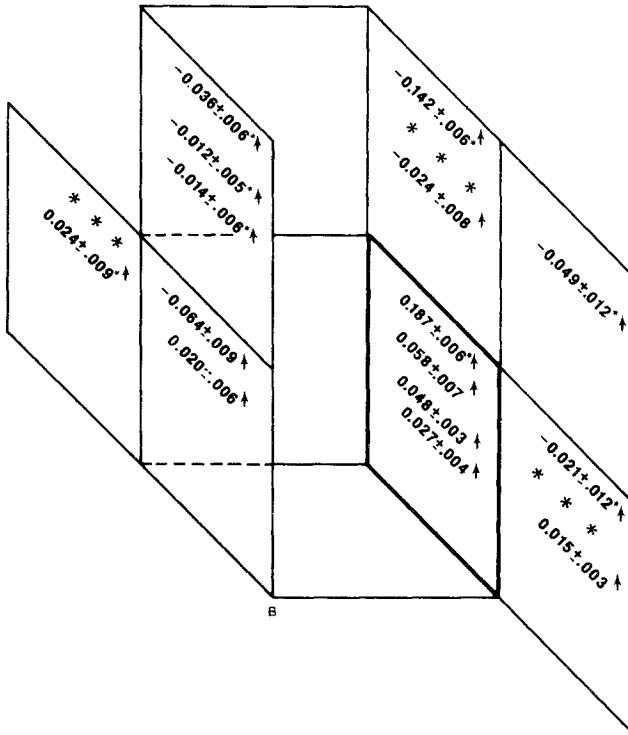
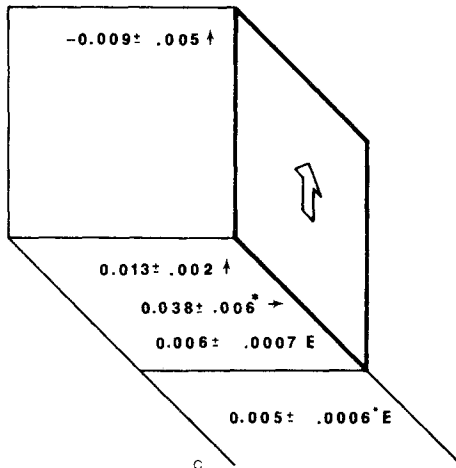


Fig. 2. Shear momentum transfer equation-of-motion parameters $B_{x;h}$, where x = shear momentum (P_y) transfer across the heavy face. Format is the same as in Fig. 1.



B



C

Fig. 2. continued.

of the variables at time m decreases rapidly as m decreases beyond $-1/2$, the spatial range broadens. This is intuitively reasonable, and has the consequence that the influences of the transfers $x(\alpha, f, m)$ across a fixed face f do not decrease monotonically as m decreases.

5. LONG-TIME TAILS

The most familiar method for obtaining transport coefficients from molecular-dynamics simulations is the Green-Kubo method. In this method each transport coefficient is expressed as a time integral of an equilibrium time-correlation function⁽⁹⁾ (a shear-shear correlation in the case of viscosity). It therefore requires knowledge of the correlation function at large times t . When the Green-Kubo technique was first proposed,⁽¹⁰⁾ this was not thought to be a serious problem, because it was thought that the correlations would die out exponentially, in one or two mean collision times. The inefficiency of the Green-Kubo method lies in the fact that this is not true; times greater than a mean collision time contribute greatly to the time integral.⁽²⁰⁾ In fact the correlation function does not die out exponentially at all; it has a power-law decay^(8,21) ($t^{-3/2}$ in three dimensions). The correlation function is therefore "nonlocal" in time (and in space as well); accurate transport coefficient calculations require simulating large systems for long times.

The essential claim we have made⁽¹⁵⁾ for the discrete equation-of-motion approach is that it is local: the transfer across a face depends only on nearby contents and nearby, recent transfers. This claim requires justification, since the equation-of-motion coefficients $B_{x,x}$ in Eq. (2.1) represent a "memory" effect of an earlier transfer on the transfer at time $1/2$. One might guess that these would have the same long-time behavior as the time correlation function, as we mentioned in Section 2. In fact, it is often said that fluid equations of motion must be nonlocal if the correlations are. This belief arises in part from study of very simple linear models⁽²²⁾ in which a non-Markoffian (i.e., nonlocal in time) time correlation function rigorously requires a non-Markoffian equation of motion ("memory function"). However, these models are so oversimplified that the generalization to a real fluid seems very risky (for example, the models lack "mode coupling," which has been shown⁽²¹⁾ to be necessary in order to obtain long-time tails in the first place). And there is definite evidence for the contrary viewpoint, that long-time tails are perfectly consistent with a local, Markoffian equation of motion. In fact in Alder and Wainwright's original paper⁽⁸⁾ demonstrating the existence of the long-time tail and its origin in long-lived "vortices" associated with a moving particle, they also showed that these phenomena could be quantitatively reproduced by

solving discretized Navier–Stokes equations (i.e., equations of motion *local* in time and space, similar in form to those of our theory).

The present numerical calculations are the first which are accurate and extensive enough to address directly the question of whether the B 's have long tails. In Fig. 3 we have plotted $B_{x(\alpha,f,1/2);x(\alpha,f,m)}$, the “tail” of the

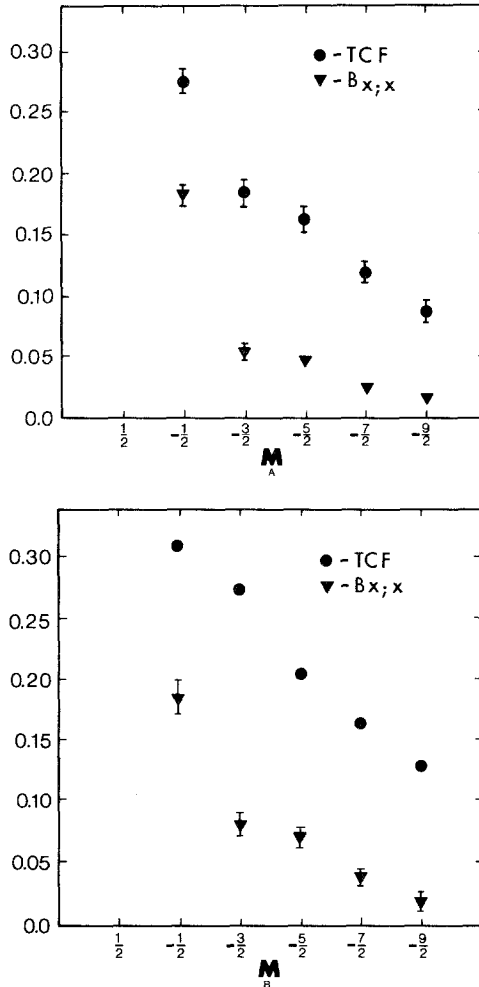


Fig. 3. Comparison of normalized time-correlation function $\langle x(\alpha, f, 1/2)x(\alpha, f, m) \rangle / \langle x(\alpha, f, 1/2)^2 \rangle$, labeled TCF, with corresponding equation-of-motion coefficients $B_{x(\alpha,f,1/2);x(\alpha,f,m)}$. Where error bars are not shown, errors are less than the symbol size. (a) Shear transfer for viscosity calculation ($\alpha = P_y$) (b) Longitudinal momentum transfer ($\alpha = P_x$).

discrete equation of motion, against the negative time m . The equation (2.2) for each of these B 's has $\langle x(\alpha, f, 1/2)x(\alpha, f, m) \rangle$ on the left-hand side. In fact, if all terms but the diagonal one ($h = h'$) are ignored on the right-hand side, one obtains the estimate $B_{x;x} \sim \langle x(\alpha, f, 1/2)x(\alpha, f, m) \rangle / \langle x(\alpha, f, m)^2 \rangle$, a normalized time correlation function. It is therefore natural to include the latter in Fig. 3 for comparison to $B_{x;x}$. It can be seen that the behaviors are markedly different. The time correlation function drops off very slowly, consistently with power-law behavior. The equation-of-motion coefficients B , on the other hand, drop off much more rapidly with time, decreasing on the average by a factor of 2 for each time interval τ . In fact, the ratio of successive B 's which best fits the data is 0.556 for shear transfer and 0.562 for longitudinal transfer.

As mentioned above, the time correlation function is expected to behave as $t^{-3/2}$ at very long times. We have not attempted to fit it to this form because it has been found previously⁽²⁰⁾ that other contributions remain important for quite a long time, perhaps as long as the 5τ we have included here. In particular, it is likely that viscoelastic effects⁽²³⁾ contribute strongly to the short-time shear-shear correlation at high densities such as we have used. Such questions are irrelevant to the fundamental conclusion which can be drawn from Fig. 3, namely, that the discrete method provides a much more rapidly convergent method for calculating the viscosity than the Green-Kubo method.

The last TCF in Fig. 3 is about five times larger than the last $B_{x;x}$. The uncertainty associated with truncating the series of TCFs is much greater than five times that associated with the B 's since TCF decreases so slowly. In fact, the advantage of calculating η from the B 's is even greater than this, since $B_{x;x}$ enters η in a qualitatively different way than the time correlation function enters the Green-Kubo η . The latter is simply the time integral of the time correlation function, i.e., essentially the sum of the discrete $\langle x(\alpha, f, 1/2)x(\alpha, f', m) \rangle$. Our expression for the viscosity, on the other hand [obtained by solving Eq. (4.1)], depends mostly on $B_{x;c}$, i.e., on the effects of cell contents (Fig. 2a). The sum of the $B_{x;x}$'s affects η by less than 20%, entering as a factor $(1 - \sum B_{x;x})^{-1}$. Thus the uncertainty introduced by truncating the TCFs is more than 25 times greater than that due to truncating the B 's.

The essential result of this paper is therefore that the discrete method effectively eliminates long-time memory behavior as the accuracy-limiting factor in viscosity calculations via molecular dynamics. The limitations of system-size dependence and cell-size dependence remain, of course, but the former is no worse than in the Green-Kubo or nonequilibrium molecular dynamics⁽¹⁹⁾ methods, and the latter appears to be a small effect⁽¹¹⁾ and can at any rate be treated precisely by renormalization techniques.^(2,12)

ACKNOWLEDGMENTS

The authors would like to thank the Chemistry Division of the National Science Foundation for support through grant No. CHE-7906649, and J. P. Straley for critical reading of the manuscript.

REFERENCES

1. P. B. Visscher, *J. Stat. Phys.* **18**:59 (1978).
2. P. B. Visscher, *Physica* **97A**:410 (1979).
3. K. G. Wilson and J. Kogut, *Phys. Rept.* **12C**:75 (1974).
4. Th. Niemeijer and J. M. J. van Leeuwen, in *Phase Transitions and Critical Phenomena*, Vol. 6, C. Domb and M. S. Green, eds. (Academic, New York, 1976).
5. D. S. Gaunt and A. J. Guttmann, in *Phase Transitions and Critical Phenomena*, Vol. 3, C. Domb and M. S. Green, eds. (Academic, New York, 1974).
6. D. L. Hunter and G. A. Baker Jr., *Phys. Rev. B* **7**:3346 (1973).
7. M. H. Ernst, L. K. Haines, and J. R. Dorfman, *Rev. Mod. Phys.* **41**:296 (1969).
8. B. J. Alder and T. E. Wainwright, *Phys. Rev. A* **1**:18 (1970).
9. B. J. Berne and Dieter Forster, *Ann. Rev. Phys. Chem.* **22**:564 (1971).
10. M. S. Green, *J. Chem. Phys.* **20**:1281 (1952); **22**:398 (1954).
11. S. Begum and P. B. Visscher, "Transport Coefficient Calculation by Discrete Hydrodynamics," preprint (University of Alabama).
12. P. B. Visscher, "Exact Fixed Points in Discrete Hydrodynamics," *J. Stat. Phys.* **25**:211 (1981).
13. P. B. Visscher, "Critical Fixed Points in Discrete Hydrodynamics," *Physica* **108A**:153 (1981).
14. S. Begum and P. B. Visscher, *J. Stat. Phys.* **20**:641 (1979).
15. P. B. Visscher, *J. Chem. Phys.* **68**:750 (1978).
16. N. R. Draper and H. Smith, *Applied Regression Analysis* (Wiley, New York, 1966); R. F. Gunst and R. L. Mason, *Regression Analysis and its Application* (Dekker, New York, 1980).
17. P. B. Visscher, *J. Stat. Phys.* **20**:629 (1979).
18. L. Verlet, *Phys. Rev.* **159**:98 (1967).
19. W. T. Ashurst and W. G. Hoover, *Phys. Rev. A* **11**:658 (1975).
20. D. Levesque, L. Verlet, and J. Kurkujarvi, *Phys. Rev. A* **7**:1690 (1973).
21. M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, *J. Stat. Phys.* **15**:7 (1976); *Phys. Rev. A* **4**:2055 (1971).
22. N. Corngold, *Phys. Rev. A* **6**:1570 (1972).
23. A. Z. Akcasu and E. Daniels, *Phys. Rev. A* **2**:962 (1970).