

## **Discrete Hydrodynamics: Numerical Results for the Soft-Sphere Viscosity**

**Salma Begum<sup>1,2</sup> and P. B. Visscher<sup>3</sup>**

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Numerical calculations have been done of the viscosity of the soft-sphere liquid, using a new molecular dynamics technique. It is based on a formulation of hydrodynamics which is discrete in space and time, and exactly renormalizable. The present data turn out to be sufficient to estimate the viscosity, but determination of the full equations of motion (and therefore renormalization) requires further calculations using a smaller discrete time interval; these are presently under way. The present results indicate that this method is more than 100 times more efficient than previous (Green-Kubo or nonequilibrium molecular dynamics) methods. This suggests that the discrete formulation is the most natural way to approach hydrodynamics.

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**KEY WORDS:** Molecular dynamics; transport coefficients; viscosity.

### **1. INTRODUCTION**

In a previous paper<sup>(1)</sup> a detailed method was described for determining discrete equations of motion for classical fluids from molecular dynamics simulation data on finite systems. In the present paper we apply this method to obtain numerically the equations of motion and small-cell ("bare") viscosity of the soft-sphere liquid ( $r^{-12}$  potential). This potential was chosen because of its simplicity and because its transport coefficients have been calculated by Ashurst and Hoover<sup>(2)</sup> using nonequilibrium molecular dynamics. The present method gives the same result, with about 200 times less calculation.

In Section 2 we describe the molecular dynamics calculation, and in Section 3 give the numerical results for the equations of motion and the bare

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<sup>1</sup> Institute of Theoretical Science, University of Oregon, Eugene, Oregon.

<sup>2</sup> Present address: Department of Physics and Astronomy, University of Alabama, University, Alabama.

<sup>3</sup> Department of Physics and Astronomy, University of Alabama, University, Alabama.

viscosity. These are calculated from the raw molecular dynamics data by a method derived in detail previously.<sup>(1)</sup> Because this derivation is quite complicated, we thought it useful in the present paper to give a very brief heuristic explanation of the method.

The discrete approach involves dividing the system into cells (labeled by  $l$ ) of width  $W$ , and dividing time into intervals of length  $\tau$ . Instead of continuum density variables, we define cell contents of the five conserved quantities:  $c_{Nlm}$ ,  $c_{Elm}$ ,  $c_{P_xlm}$ , ... (these are contents at time  $m\tau$ ,  $m = \text{integer}$ ). The analogs of the continuum fluxes are the transfers, denoted  $x_{Nfm}$ ,  $x_{Efm}$ , ... (transfers across face  $f$  in a time interval labeled by  $m$ ). The theory predicts the transfer in the interval  $(0, \tau)$  from the history at times  $t \leq 0$  by the equation of motion

$$[x_j] = \sum_k B_{j;k} h_k \quad (1.1)$$

where  $j$  and  $k$  are composite indices representing  $(Nlm)$  or  $(Nfm)$ , etc.;  $h_k$  is a history variable (usually a content at  $t = 0$ , but possibly a transfer at  $t < 0$ ). (For present purposes we ignore the constant term, nonlinear terms, and fluctuations included in the general theory; our numerical results do not involve these.) All of the (nonequivalent) equation-of-motion coefficients we calculated numerically are defined in Table I (also see Fig. 1), and given arbitrary integer labels  $\beta = 8, 30, \dots$ , so  $B_{j;k}$  can be referred to concisely as  $B_\beta$ . Each  $B_{j;k}$  describes the influence of a history variable  $h_k$  on an expected transfer  $x_j$ ; for example,  $B_8$  describes the effect of the vertical momentum content of a cell at  $t = 0$  on the flux of vertical momentum out the side of the cell (the shear transfer). Note that we consider only the system of  $B$ 's involved in predicting the shear transfer (which are related to the viscosity); these can be calculated independently of all others, as shown in Ref. 1.

These equation-of-motion coefficients  $B$  are to be calculated from

**Table I. Nonequivalent Equation-of-Motion Coefficients  $B_{j;k}$**

Label $\beta$	Index $j(\beta)$	Index $k(\beta)$
8	$P_y, f, 1/2^a$	$P_y, l_1, 0$
59	$P_y, f, 1/2$	$P_y, l_2, 0$
62	$P_y, f, 1/2$	$P_y, l_3, 0$
30	$P_y, f, 1/2$	$P_y, f, -1/2^b$
110	$P_y, f, 1/2$	$P_y, f, -3/2$

<sup>a</sup> The label  $m = 1/2$  denotes the time interval  $(0, \tau)$ .

<sup>b</sup> The previous transfer, in the interval  $(-\tau, 0)$ .

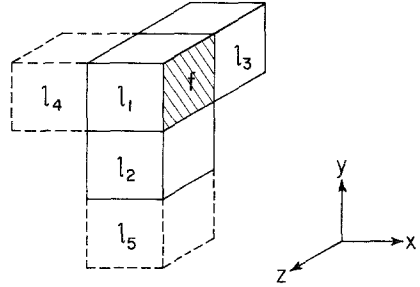


Fig. 1. Meanings of cell and face labels used in Tables I and II.

ensemble averages (denoted  $\langle v_j v_k \rangle$ , where  $v_j$  and  $v_k$  are any cell variables), which are estimated by averaging molecular dynamics data. The nonequivalent averages we have calculated are listed in Table II, labeled by an integer  $\gamma$  so we may refer to them as  $\langle v_\gamma \rangle$ . If we multiply Eq. (1.1) by a history variable  $h_{k'}$  and ensemble-average, we get

$$\langle x_j h_{k'} \rangle = \sum_{k'} B_{j;k'} \langle h_k h_{k'} \rangle \tag{1.2}$$

which we regard as an equation for  $B_{j;k'}$ . For example, the equation for  $B_8$  is

$$\langle v_8 \rangle = B_8 \langle v_{15} \rangle + 2B_{59} \langle v_{19} \rangle + 2B_{62} \langle v_{22} \rangle - B_8 \langle v_{22} \rangle - \dots \tag{1.3}$$

The integer coefficients arise from symmetry considerations discussed in detail in Ref. 1. All the terms we use in Eq. (1.2) are given in Table III, which lists

Table II. Nonequivalent Cell-Variable Averages

Label $\gamma$	First index <sup>a</sup> $j_1'(\gamma)$	Second index <sup>a</sup> $j_2'(\gamma)$	Importance <sup>b</sup> $\langle v_\gamma \rangle \partial \eta_0 / \partial \langle v_\gamma \rangle$
8	$P_y, f, 1/2$	$P_y, l_1, 0$	0.739
59	$P_y, f, 1/2$	$P_y, l_2, 0$	0.881
62	$P_y, f, 1/2$	$P_y, l_3, 0$	0.098
30	$P_y, f, 1/2$	$P_y, f, -1/2$	0.313
110	$P_y, f, 1/2$	$P_y, f, -3/2$	0.028
15	$P_y, l_1, 0$	$P_y, l_1, 0$	-1.582
19	$P_y, l_1, 0$	$P_y, l_2, 0$	0.108
22	$P_y, l_1, 0$	$P_y, l_3, 0$	-0.055
72	$P_y, l_2, 0$	$P_y, l_3, 0$	-0.099
76	$P_y, l_3, 0$	$P_y, l_4, 0$	-0.003
48	$P_y, f, -1/2$	$P_y, f, -1/2$	-0.426
111	$P_y, f, 3/2$	$P_y, l_1, 0$	-0.001

<sup>a</sup> Notation chosen to conform with Ref. 1.

<sup>b</sup> The importance of average  $\gamma$  to the bare viscosity [Eq. (3.2)] for the  $\tau = 0.419, 3 \times 3 \times 3$  system of Section 3.

Table III. Nonequivalent Terms in Eq. (1.2)

Term number $\mu$	Equation label $\beta'$	$B_{j;k}$ label <sup>a</sup> $\beta(1)$	$\langle h_k h_{k'} \rangle$ label <sup>a</sup> $\gamma(1')$	Symmetry coefficient <sup>b</sup> $C_\mu$	Importance $T \partial\eta_b/\partial T$
1	8	8	15	1	0.669
2	8	59	19	2(1)	0.039
3	8	62	22	2(1)	-0.004
4	8	8	22	-1	0.025
5	8	59	72	-2(-1)	0.036
6	8	62	76	-2(-1)	0.003
7	8	30	8	-1	0.075
8	8	110	111	-1	0.001
9	59	59	15	1	0.818
10	59	8	19	1	-0.061
11	59	59	22	-1	0.030
12	59	8	72	-1	0.056
13	59	30	59	-1	-0.091
14	62	62	15	1	0.094
15	62	62	22	-1	0.004
16	62	30	62	-1	-0.011
17	30	30	48	1	0.398
18	30	8	8	-2	-0.048
19	30	59	59	-4(-2)	-0.038
20	30	110	30	1	0.006
21	110	8	111	-2	0.001
22	110	110	48	1	0.027

<sup>a</sup> Notation conforms with Ref. 1.

<sup>b</sup>  $C_\mu$  for  $2 \times 2 \times 2$  system is given in parentheses if different from  $3 \times 3 \times 3$  values.

for each term (numbered by  $\mu$ ) which equation it is in (that for  $B_{\beta'}$ ), the labels of its two factors  $B_{j;k}$  and  $\langle h_k h_{k'} \rangle$ , and its coefficient  $C_\mu$ . The first four rows reproduce Eq. (1.3).

Equation (1.2) must be solved by successive approximation. This means we need a strategy for deciding which  $B$ 's to calculate and which terms to include; the test of such a strategy is the rapidity with which some desired result (e.g., the bare viscosity  $\eta_b$ ) converges as the number of terms increases. Repeating the calculation each time a new term is included is a tedious procedure; it has been found more useful to analytically calculate the "importance" of the  $\mu$ th term (call it  $T_\mu \equiv C_\mu B_{j;k} \langle h_k h_{k'} \rangle$ ) defined as  $T_\mu \partial\eta_b/\partial T_\mu$  (with other terms held constant). This is essentially the error caused by leaving out the term (unless this is large). We have included these importances in Table III, calculated for the  $3 \times 3 \times 3$  system with  $\tau = 0.419$  discussed in Section 3 (they are similar for the  $2 \times 2 \times 2$  system except that

terms involving averages such as  $\gamma = 72$  with a strong size dependence are more important). One can also define an importance for each average  $\langle v_\gamma \rangle$ , namely  $\langle v_\gamma \rangle \partial \eta_b / \partial \langle v_\gamma \rangle$ ; this is the error caused by leaving out the average, and is given in Table II. Our actual term-choosing strategy is mostly intuitive. However, the calculated importances seem to confirm intuition, in that averages involving variables far apart in space ( $\gamma = 76$ ) or time ( $\gamma = 110, 111$ ) are unimportant. It seems likely that those not included (because they are even further apart) will not change  $\eta_b$  much. We have also done calculations including a nonlinear convective term,<sup>(3,4)</sup> which did not change the result. We believe that the truncation error is small compared to the statistical uncertainties described in Section 3.

To obtain transport coefficients from  $B$ 's, we transform them into "excess-transfer" coefficients<sup>(3)</sup>  $\tilde{B}$ . These are defined by an equation [say (1.1')] identical to (1.1) except that the history variables  $h_k$  are contents and excess transfers

$$\Delta x_j \equiv x_j - [x_j] \quad (1.4)$$

This has the advantage that when the cells are large (and fluctuations small)  $\Delta x_j \simeq 0$  in a steady-state system and  $B$  is easy to relate to transport coefficients; in particular the viscosity is<sup>(3)</sup>

$$\eta = -m\rho(W^2/\tau) \sum_l (I - \mathbf{f}) \tilde{B}_{P f \frac{1}{2}; P l 0} \quad (1.5)$$

where  $l$  denotes the coordinates of the center of cell  $l$  (in units of  $W$ , so  $l$  is dimensionless),  $\mathbf{f}$  denotes the center of face  $f$ , and  $P$  is the momentum component transverse to  $f$ . When the cells are not large, we will refer to Eq. (1.5) as the "bare" viscosity; the cells of Section 3 appear to be large enough so there is not much difference.

Equations for the excess-transfer coefficients  $\tilde{B}$  may be obtained by substituting Eq. (1.1) into (1.4), (1.4) into (1.1'), and equating the resulting power series in contents and transfers term by term to Eq. (1.1). Using only the  $B$ 's listed in Table I (and the corresponding  $\tilde{B}$ 's), the result is

$$\begin{aligned} B_8 &= \tilde{B}_8 - \tilde{B}_{30} B_8 - \tilde{B}_{110} B_8 \\ B_{59} &= \tilde{B}_{59} - \tilde{B}_{30} B_{59} - \tilde{B}_{110} B_{59} \\ B_{62} &= \tilde{B}_{62} - \tilde{B}_{30} B_{62} - \tilde{B}_{110} B_{62} \\ B_{30} &= \tilde{B}_{30} - 2\tilde{B}_{30} B_8 - 2\tilde{B}_{110} B_8 \\ B_{110} &= \tilde{B}_{110} - \tilde{B}_{30} B_{30} - 2\tilde{B}_{110} B_8 \end{aligned} \quad (1.6)$$

These equations are used to determine  $\tilde{B}$  in Section 3.

## 2. MOLECULAR DYNAMICS CALCULATION

Calculation of the equation-of-motion parameters  $B$  from Eq. (1.2) requires knowing equilibrium averages of products of all variables; contents

$c_{Nlm}, \dots$  and transfers  $x_{Nfm}, \dots$ . We have calculated these variables by molecular dynamics, i.e., by numerically integrating Newton's second law for  $N$  ( $= 32$  or  $108$ ) particles in a finite system (a periodic cube). In the soft-sphere liquid<sup>(5,6,2)</sup> the particles interact via the central potential

$$\Phi(r) = \epsilon s^{12}/r^{12} \quad (2.1)$$

Here  $s$  is an effective hard-core radius, and  $\epsilon$  sets the energy scale. Our numerical results will be quoted in the usual<sup>(2)</sup> system of units in which  $\epsilon$ ,  $s$ , and  $m$  (the particle mass) are the units of energy, length, and mass.

By taking time averages of the cell variables (and assuming ergodicity) one obtains averages in a microcanonical ensemble (with fixed total momentum, energy, and number of particles). As the system size and total averaging time increase (while number density  $\rho = N/V$  and energy density  $e = E/V$  remain constant), these averages, and the equations of motion obtained from them, should approach those of a thermodynamic system with this  $\rho$  and  $e$ , which we wish to calculate. Because the most accurate equilibrium equation-of-state calculations have been done using the Monte Carlo method,<sup>(6)</sup> for which the natural variable is the temperature  $T$ , rather than  $e$ , we shall specify the thermodynamic state of our system by  $T$  and  $\rho$ .

Because of the extremely simple power-law form of the soft-sphere potential, the properties of the system throughout the  $T, \rho$  phase plane can be obtained from a single isotherm by a scale transformation.<sup>(5)</sup> We therefore need only do calculations for a single temperature, which we may as well choose to be  $kT = \epsilon$ , our unit of energy. The properties will then depend on  $\rho$  only, which is commonly<sup>(2,5)</sup> specified by a dimensionless "reduced density"

$$\rho_{\text{red}} \equiv \rho s^3 / \sqrt{2} \quad (2.2)$$

It has been previously found<sup>(2)</sup> that for  $\rho_{\text{red}} < 0.2$ , kinetic theory (in particular the Enskog theory applied to an "equivalent" hard-sphere system) gives good results. As  $\rho_{\text{red}}$  increases toward the freezing point ( $\rho_{\text{red}} = 0.813$ ), the discrepancy between Enskog theory and the molecular dynamics viscosity gets quite large. By  $\rho_{\text{red}} = 0.6$  it is already 50%; we have chosen this value for our calculation, to test the new method in a region where kinetic theory fails.

The molecular dynamics calculation we have done is quite standard,<sup>(7,2)</sup> except for the analysis of the results in terms of cell variables: we shall therefore emphasize the latter here. We used the simplest possible integration algorithm (due to Verlet<sup>(7)</sup>), which integrates first-order equations for positions  $\mathbf{r}_i(t)$  and velocities  $\mathbf{v}_i(t)$  by the central-difference method:

$$\begin{aligned} \mathbf{v}_i(\tfrac{1}{2} \Delta t) &= \mathbf{v}_i(-\tfrac{1}{2} \Delta t) + \Delta t \mathbf{F}_i(0)/m \\ \mathbf{r}_i(\Delta t) &= \mathbf{r}_i(0) + \Delta t \mathbf{v}_i(\tfrac{1}{2} \Delta t) \end{aligned} \quad (2.3)$$

Thus the positions are known at integral multiples of the integration increment  $\Delta t$ , and the velocities at half-integer multiples. The differencing errors in the positions introduced by this algorithm are of order  $(\Delta t)^3$ ,<sup>(8)</sup> but those in the velocities are of order  $(\Delta t)^2$ .

The integration was started with random velocities but regular positions (an fcc lattice). We need to achieve a certain temperature  $T$  ( $T = 1.0$  in our units); however, since  $T$  (defined in terms of the kinetic energy) fluctuates in the microcanonical ensemble, and very accurate equation-of-state data relating  $T$  to the energy exists,<sup>(6)</sup> we chose to fix our energy at the value  $3.61\epsilon$  per particle given by Ref. 6 for  $\rho_{\text{red}} = 0.6$  and a 32-particle system (the  $N = \infty$  value quoted is almost identical). This provides a check on our program, since the kinetic energy per particle should be exactly 1.5 in an infinite system; calculated averages were  $1.476 \pm 0.010$  (32 particles, total time  $1980 \Delta t$ ) and  $1.494 \pm 0.004$  (108 particles,  $1530 \Delta t$ ). The consistency and convergence appear to be extremely good. (All errors are estimated from the scatter of partial-run averages.) Initial equilibration (i.e., melting of the fcc lattice) was accelerated by starting with too high a kinetic energy (by about 40%), integrating for about  $50 \Delta t$ , lowering the energy to the desired value by scaling down the velocities, and equilibrating again for about  $30 \Delta t$ . Judging from the rate of relaxation of the kinetic energy to its equilibrium value, these equilibration times seem ample. In order to calculate averages of contents and transfers, we must of course pick the cell width  $W$  and the time interval  $\tau$ . It is extremely convenient to choose  $W$  so that the average number of particles per cell

$$N_c \equiv \rho W^3 \quad (2.4)$$

is an integer (so we can approach the thermodynamic limit by adding more cells to the system without getting fractional  $N$ ). So in practice we choose  $N_c$  and  $\tau$ , and determine  $W$  from Eq. (2.4). We have used the value  $N_c = 4$ , which is large enough for us to expect "hydrodynamic" behavior (i.e., fluctuations are not too large) but small enough that the computer (a PDP-10) can easily handle systems of  $2 \times 2 \times 2$  cells ( $N = 32$ ) and  $3 \times 3 \times 3$  cells ( $N = 108$ ). It has the additional advantage that an fcc lattice can be used for initialization. This choice gives [using  $\rho = 0.849s^{-3}$  from Eq. (2.2)]  $W = 1.677s$ .

Once  $W$  is chosen, a natural time interval can be obtained by dividing by the velocity unit (proportional to thermal velocity):  $W/(\epsilon/m)^{1/2}$  measures the time required for a free particle to cross a cell. Since hydrodynamic disturbances may move somewhat faster, we did calculations using  $1/2$  and  $1/4$  of this as  $\tau$  [ $\tau = 0.838s(\epsilon/m)^{-1/2}$  and  $0.419s(\epsilon/m)^{-1/2}$ ]. As we discuss below, it turns out that an even smaller value would have been preferable; such calculations are now under way.

It remains only to specify the integration increment  $\Delta t$ . Obviously

this should be a submultiple of the interval  $\tau$  between content determinations; we chose  $\Delta t = 0.01048s(\epsilon/m)^{-1/2}$  (1/40 of the smaller  $\tau$  above), because it is close to the value of  $\Delta t = 0.01006$  used by Ashurst and Hoover for  $N = 108$  and facilitates comparison with their results.

As we integrate the equations of motion we also compute the cell contents and transfers; the algorithm used for this is described in the Appendix. The result is a magnetic tape with 540 contents and transfers (for the 27-cell case) per interval  $\tau$ . Averages of products (including those listed in Table II) were calculated by averaging over time, rotations and translations as described in Ref. 1, leading to the numerical results (Table IV) analyzed in the next section.

### 3. NUMERICAL RESULTS

Our initial molecular dynamics calculations used  $W = 1.677$ ,  $\tau = 0.838$  [units are  $s$  and  $s(\epsilon/m)^{-1/2}$ ] as described in Section 2. Since the registry of the cell structure with respect to the trajectories is arbitrary, one can extract additional information from a set of trajectories by displacing them uniformly and recomputing the contents and transfers. This is most easily done by calculating contents and transfers for smaller cells ( $W = 0.838$ ), which can be combined into larger cells in eight different ways. By using a smaller  $\tau$  (0.419) we similarly obtained data for two sets of time-translated trajectories. If all of these 16 sets of data were independent, this would decrease the statistical error by  $\sqrt{16} = 4$ . In fact the errors (i.e., standard deviations of the mean obtained by dividing the run into four segments, averaged separately) decreased on the average by a factor of two, so the procedure appears worthwhile.

The first two columns of Table IV give the cell-variable averages obtained from calculations of length  $3000\Delta t$  ( $2 \times 2 \times 2$  system) and  $1200\Delta t$  ( $3 \times 3 \times 3$  system). Equations (1.2) were solved for the  $B$ 's; these are given in first two columns of Table V. It appears that this  $\tau$  was too long, allowing contents of distant cells like  $l_4$  (Fig. 1) to affect the transfer (so that  $B$ 's not listed in Table I contribute significantly to the viscosity). The large size of the  $B$  coefficients suggests that we ought to worry about this; if one imagines putting extra vertical momentum in a vertical column of cells, the equation of motion implies that a large fraction  $F^3 = 0.844$  (or  $F^2 = 0.812$  in the  $2 \times 2 \times 2$  system) will leave the column during  $\tau$ , where

$$F^2 \equiv 4B_8^2 + 4B_{59}^2, \quad F^3 \equiv 4B_8^3 + 8B_{59}^3 \quad (3.1)$$

It is certainly possible that some might cross more than one cell. One symptom would be that in small systems, momentum would feed back into the column from nearby images, making  $F^2 < F^3$  (which it is). Another symptom would



Table IV. Numerical Results for Averages, for  $W = 1.677$ , in  $2 \times 2 \times 2$ - and  $3 \times 3 \times 3$ -Cell Systems

Label $\gamma$	$\tau = 0.838$		$\tau = 0.419$	
	$2 \times 2 \times 2$	$3 \times 3 \times 3$	$2 \times 2 \times 2$	$3 \times 3 \times 3$
8	0.417	0.326	$0.379 \pm 0.033$	$0.331 \pm 0.026$
59	0.352	0.216	$0.357 \pm 0.007$	$0.208 \pm 0.012$
62	0.126	0.058	$0.057 \pm 0.041$	$0.025 \pm 0.018$
30	0.843	0.587	$0.445 \pm 0.056$	$0.416 \pm 0.055$
110	0.637	-0.044	$0.126 \pm 0.045$	$0.087 \pm 0.016$
15	3.544	3.815	$3.552 \pm 0.043$	$3.830 \pm 0.080$
19	-0.394	-0.225	$-0.384 \pm 0.074$	$-0.178 \pm 0.094$
22	-0.528	-0.119	$-0.530 \pm 0.048$	$-0.142 \pm 0.052$
72	-0.502	-0.163	$-0.502 \pm 0.036$	$-0.163 \pm 0.030$
76	-0.497	-0.115	$-0.496 \pm 0.034$	$-0.115 \pm 0.061$
48	9.902	9.494	$4.479 \pm 0.060$	$4.283 \pm 0.024$
111	0.050	-0.012	$0.013 \pm 0.027$	$-0.014 \pm 0.015$

be that the estimate Eq. (3.2) of the viscosity (in which these distant  $B$ 's would have three times the weight of those we have included) would be low (and it is, by a factor of two).

We therefore reanalyzed the data, using the smaller  $\tau = 0.419$ , obtaining the averages in the right half of Table IV. The resulting  $B$ 's and  $\tilde{B}$ 's from Eqs. (1.2) and (1.6) are given in Table V. The best estimates  $\tilde{B}^{\infty, M}$  (from  $M \times M \times M$  system data) given in the last two columns are obtained by taking account of image effects via Eq. (4.4) of Ref. 1. [They differ from  $\tilde{B}^M$  only in that  $\tilde{B}_{59}^2 = 2\tilde{B}_{59,2}^2$  and  $\tilde{B}_{62}^2 = 2\tilde{B}_{62,2}^2$ , because the effect of cell  $l_2$  or  $l_3$  (Fig. 1) is doubled by its periodic image on the opposite side of  $l_1$  in a  $2 \times 2 \times 2$  system.] It is interesting that  $F^3 = 0.864$ , still about as large as for the larger  $\tau$ . Thus all the momentum leaving the column mentioned above left in the first half of the interval (reinforcing the conclusion that the earlier  $\tau$  was too large). On the other hand,  $\tilde{B}_{62}$  is getting small, indicating that shear momentum has not traveled very far during  $\tau = 0.419$ , so it is likely that the  $B$ 's in Table I are sufficient for obtaining the bare viscosity. A purely diffusive model for the leakage of momentum from a column requires much more spreading before such depletion of the column; a proper intuitive picture probably involves shear wave propagation as well. The bare viscosity is given by Eq. (1.5), which (using  $\tau = 0.419$  and the  $B$ 's in Table I) becomes

$$\eta_b = 5.695[(\epsilon m)^{1/2}/s^2](\tilde{B}_8 + 2\tilde{B}_{59} + 2\tilde{B}_{62}) \tag{3.2}$$

This is given at the bottom of Table V. It will be noted that the size dependence of the viscosity is very small (less than 4%), whereas the size dependences of  $\tilde{B}_8$  and  $\tilde{B}_{59}$  are much larger (10 or 20%). This is evidently

Table V. Numerical Results for Equation-of-Motion Coefficients and Bare Viscosity<sup>a</sup>

Label $\beta$	$\tau = 0.838$						$\tau = 0.419$		
	$B_\beta^2$	$B_\beta^3$	$B_\beta^2$	$B_\beta^3$	$\tilde{B}_\beta^2$	$B_\beta^3$	$\tilde{B}_\beta^{\infty,2b}$	$\tilde{B}_\beta^{\infty,3b}$	
8	0.111	0.091	0.102	0.126	0.126	0.094	0.126 ± 0.010	0.113 ± 0.004	
59	0.092	0.060	0.096	0.118	0.118	0.059	0.059 ± 0.002	0.071 ± 0.002	
62	0.034	0.016	0.016	0.020	0.020	0.007	0.010 ± 0.007	0.008 ± 0.005	
30	0.098	0.074	0.129	0.170	0.170	0.121	0.170 ± 0.008	0.155 ± 0.014	
110	0.033	-0.005	0.029	0.064	0.064	0.020	0.064 ± 0.015	0.048 ± 0.004	
$\eta_b(s^2/(\epsilon m)^{1/2})$	—	—	—	—	—	—	1.492 ± 0.098	1.548 ± 0.069	

<sup>a</sup> The superscript  $M$  on the  $B$ 's refers to the number of cells ( $M \times M \times M$ ) in the system.

<sup>b</sup> Uncertainties obtained from scatter of  $B$ 's calculated from shorter-run averages, not by propagating errors in averages (which incorrectly assumes they are independent). Uncertainties in left-hand columns are similar, and have been omitted.

because  $\tilde{B}_8$  and  $\tilde{B}_{59}$  are sensitive to the longitudinal propagation of momentum, which  $\eta$  is not. In fact, if the  $\tilde{B}_\beta$  describing momentum from cell  $l_5$  in Fig. 1 crossing face  $f$  were nonzero (in the infinite system), through its images it would increase  $\tilde{B}_8$  by  $2\tilde{B}_\beta$  in the  $2 \times 2 \times 2$  system and  $\tilde{B}_{59}$  by  $\tilde{B}_\beta$  in the  $3 \times 3 \times 3$  system (thus leaving  $\eta_b$  size-independent). Exactly this effect is apparent in Table V. This rapid longitudinal momentum propagation may be understood by noting that the sound velocity is<sup>(6)</sup> about  $v_s = 5.5(\epsilon/m)^{1/2}$ , so  $v_s\tau = 1.4W$ . This means a disturbance can travel more than the distance from  $l_5$  to  $f$  during  $\tau$ . We conclude that even  $\tau = 0.419$  is not small enough for Table I to be sufficient to describe the complete equations of motion: to describe sound waves we must either enlarge Table I (and our system) or decrease  $\tau$ . The latter is probably easier, and such calculations are under way. However, this difficulty does not interfere with the present objective [calculating the bare viscosity  $\eta_b$ , Eq. (3.2)]. This is only sensitive to transverse momentum propagation, which is sufficiently slow (as evidenced by the remarkable size independence of  $\eta_b$ ) that it does not create image problems. This is not unexpected; transverse wave velocities in solids (where they are well defined) are slower than longitudinal ones.

The bare viscosity involves only the first three  $\tilde{B}$  coefficients in Table I. The next,  $\tilde{B}_{30}$ , may be seen to be related to elasticity effects. Elastic behavior in solids occurs when a shear flux is proportional to strain. In liquids, where shear flux and strain *rate* are normally proportional (viscous behavior), "elastic" effects important on very short time scales may be included<sup>(9,8)</sup> by adding a term in the time derivative of the shear flux to the strain rate. The discrete analog of such an equation relates a linear combination of shear transfers at different times (say  $\frac{1}{2}\tau$  and  $-\frac{1}{2}\tau$ ) to the momentum contents of adjacent cells. This differs from the purely viscous equation of motion by having  $B_{j;k}$  in which  $x_k$  is a transfer at  $m = -\frac{1}{2}$ . Such terms (such as  $B_{30}$ ) may thus be thought of as "elasticity" terms.

The last coefficient  $B_{110}$  in Table I represents a non-Markovian effect. It should be stressed that  $B_{30}$ , though it describes the effect of a variable at  $t < 0$ , is not non-Markovian in the generally accepted sense. A continuum equation of motion is still regarded as "Markovian" if its evolution depends on fluxes as well as densities<sup>(9)</sup> at  $t = 0$ ; the fact that in a discrete theory the flux is necessarily averaged over  $-\tau < t < 0$  does not seem to justify changing the terminology.

#### 4. DISCUSSION

We have calculated the bare viscosity of the soft-sphere liquid, obtaining for a 108-particle system  $\eta_b = (1.55 \pm 0.07)(\epsilon m)^{1/2}/s^2$ . The quoted uncertainty is obtained from statistical fluctuations; there are two other sources

of error, namely truncation [of Eqs. (1.2) and (1.6)] and system-size effects. A feeling for the truncation error may be obtained from the importances in Tables II and III. Only 6 of the 22 terms in Table III have importances exceeding the statistical error in  $\eta_b$ ; we believe that the truncation error is certainly comparable to, and probably less than, the statistical error. The same appears to be true of the size-effect error; Table V indicates extremely rapid convergence with respect to system size  $M$ . It is much more rapid than is achievable by Green-Kubo<sup>(10)</sup> or nonequilibrium molecular dynamics<sup>(2,11)</sup> calculations, in which useful information is essentially unobtainable from systems with as few as 32 particles.

Another uncertainty appears if one wishes to compare our results with other calculations; the renormalization correction. An exact procedure for renormalization has been given in Ref. 3, and the correction will be worked out explicitly when calculations are done with a smaller  $\tau$ ; however, comparison to the result of Ashurst and Hoover<sup>(2)</sup> for the macroscopic viscosity ( $\eta = 1.5 \pm 0.1$ ) indicates that the correction is likely to be quite small. Assuming that it does not contribute disproportionately to the error, we may make an efficiency comparison between the present method and that of nonequilibrium molecular dynamics (and indirectly with the Green-Kubo method, which is generally less efficient<sup>(10)</sup>). Ashurst and Hoover sheared a 108-particle system at four different rates, each for  $32,000 \Delta t$ , and extrapolated to zero shear rate. This  $128,000 \Delta t$  is to be compared to the present  $1200 \Delta t$ , which produced a somewhat smaller error; the efficiency ratio is therefore about 200.

This very large difference in efficiency can be understood by noting that the discrete method involves calculating small-scale, short-time averages only; these are all we need to determine the small-cell equation-of-motion parameters  $B$ . This equation of motion determines the large-scale motion through the exact renormalization transformation,<sup>(3)</sup> but large-scale fluctuations need *not* be simulated in the molecular dynamics calculation. It is these fluctuations ("eddies") that introduce large statistical uncertainties into Green-Kubo results, and produce the related "long-time tail" in time-correlation functions. It is not expected that there is a non-Markovian tail in the  $B$  coefficients (for reasons discussed in detail elsewhere<sup>(12)</sup>), but unfortunately the present calculation is not accurate enough to provide independent numerical verification of this. The truncation errors in small  $B$ 's like  $B_{110}$  are probably much larger than the statistical errors given in Table V, unlike the situation for  $\eta_b$ .

It should be noted that in the discrete approach, non-Markovian memory effects are *not* particularly important in determining the viscosity. The effect of  $B_{110}$  (or the corresponding "time correlation function"  $\langle v_{110} \rangle$ ) on the bare viscosity is very small, as can be seen from Table II. And these terms do not appear to strongly influence the renormalization, which is mostly due to

nonlinear terms.<sup>(3,4)</sup> This contradicts what one would expect by superficial analogy with the Green-Kubo method; it appears the techniques are not closely analogous.

In conclusion, it appears that discrete hydrodynamics provides a qualitatively improved method for calculating the soft-sphere viscosity. The method is applicable to any fluid transport property, and may allow accurate calculations of such properties in a wide variety of systems.

## APPENDIX. ALGORITHM FOR COMPUTING CONTENTS AND TRANSFERS

In the course of the molecular dynamics calculation, we wish to calculate the contents (at each multiple of  $\tau$ ,  $t = m\tau$ ) and the transfers [over each interval ( $m\tau, m\tau + \tau$ )]. We describe here a reasonably simple algorithm for doing this to  $O(\Delta t^2)$  [more precisely, the errors in the microcanonical averages are  $O(\Delta t^2)$ ; individual transfers and contents can be changed discontinuously by an arbitrarily small change in  $\Delta t$  if a particle just on one side of a face is nudged to the other side; thus the errors cannot be bounded by a multiple of  $\Delta t^2$ ]. It appears that calculation to  $O(\Delta t^3)$  or higher would be quite complicated; there may therefore be little point in going beyond the Verlet algorithm in calculating the trajectories.

The calculation of the contents is relatively straightforward; after every  $\tau/\Delta t$  time steps one computes the momentum, energy, and number contents of each cell by adding up  $mv_i$ ,  $\frac{1}{2}mv_i^2 + U_i$ , and 1, respectively, for the particles  $i$  in the cell. The potential energies  $U_i$  of the particles are computed by assigning half of each pair potential to each particle involved. Since Verlet's algorithm only gives  $v_i$  at half-integer multiples of  $\Delta t$ ,  $v_i(t)$  is interpolated from  $v_i(t - \Delta t/2)$  and  $v_i(t + \Delta t/2)$ .

The transfers require calculations at every time step. They have two contributions: "molecular" transfers (momentum, energy, and number carried across faces by particles) and "collisional" transfers (momentum and energy only) transferred through the interatomic force between particles on opposite sides of a face. The molecular transfers are incremented each time a new position is calculated for a particle, if its new cell differs from its old one. The transfers are  $mv_i$ ,  $\frac{1}{2}mv_i^2 + U_i$ , and 1. They occur sometime in the previous interval  $\Delta t$ . Rather than try to calculate the precise time, we compute them at the *middle* of the interval. This introduces an error of order  $\Delta t$  in the transfer (for example, if the particle is accelerating and crosses the face near the beginning of the interval, we will overestimate the momentum transfer). However, if it crossed near the end of the interval, we would get an underestimate; a careful calculation shows that the effect cancels in the microcanonical averages (in fact, it already cancels if we average over time

displacements of a single trajectory). The averages are correct to  $O(\Delta t^2)$ . This procedure requires the velocities at the middle of the interval, which are fortunately known; the positions are not, and must be linearly interpolated to calculate the potential energy  $U_i$ .

The force  $\mathbf{F}_{ij}$  between each pair of interacting particles  $i$  and  $j$  contributes to the collisional transfers a momentum transfer

$$\int \mathbf{F}_{ij} dt \quad (\text{A1})$$

and an energy transfer

$$\int \frac{1}{2}(\mathbf{v}_i + \mathbf{v}_j) \cdot \mathbf{F}_{ij} dt \quad (\text{A2})$$

(signs are chosen so  $\mathbf{F}_{ij}$  acts on  $i$ , and transfers are from  $j$  to  $i$ ). We shall take the transfer to occur in a straight line, i.e., at any time  $\mathbf{F}_{ij}$  is contributing to transfers across all faces crossed by a line segment from  $\mathbf{r}_j$  to  $\mathbf{r}_i$ . Since  $\mathbf{F}_{ij}$  is computed at multiples of  $\Delta t$ , clearly we wish to approximate Eq. (A1) (integrated over  $m\tau < t < m\tau + \tau'$ ) by

$$\Delta t [\frac{1}{2}\mathbf{F}_{ij}(m\tau) + \mathbf{F}_{ij}(m\tau + \Delta t) + \dots + \frac{1}{2}\mathbf{F}_{ij}(m\tau + \tau)] \quad (\text{A3})$$

This is correct to  $O(\Delta t^2)$ . A similar form is used for Eq. (A2), except that  $\mathbf{v}(t)$  is not known when  $t$  is a multiple of  $\Delta t$ ; in fact one cannot even interpolate, because  $\mathbf{v}(t + \frac{1}{2}\Delta t)$  is not yet known [and storing all  $\frac{1}{2}N(N+1)$  of the  $\mathbf{F}_{ij}$  until it is known is prohibitive]. Therefore we extrapolate linearly from  $\mathbf{v}(t - \frac{3}{2}\Delta t)$  and  $\mathbf{v}(t - \frac{1}{2}\Delta t)$ ; this is still correct to  $O(\Delta t^2)$ .

In the computer algorithm, the contribution  $\mathbf{F}_{ij}(n\Delta t)$  to Eq. (A3) for each face  $f$  is computed when  $\mathbf{F}_{ij}$  is; the faces between  $\mathbf{r}_j$  and  $\mathbf{r}_i$  are enumerated at each  $n\Delta t$ . (Note that even for potentials with range less than the cell width  $W$ , as many as three faces, mutually perpendicular, may be crossed.) The limits on the integrals (A1) and (A2) (which should be when the segment  $\mathbf{r}_j$  to  $\mathbf{r}_i$  ceases to cross  $f$ , either by passing an edge of  $f$  or because  $r_i$  or  $r_j$  crosses  $f$ ) are automatically accounted for by this procedure; each limit is approximated by the middle  $n\Delta t + \frac{1}{2}\Delta t$  of the interval in which it lies. This introduces an error of order  $\Delta t$  in the transfer, but like the error in the molecular transfer discussed above, it cancels from the ensemble average (in fact the part due to  $r_i$  or  $r_j$  crossing  $f$  happens to cancel the molecular-transfer error even before the ensemble averaging).

Knowledge of the contents and transfers provides some checks on the correctness of the program. They satisfy exact continuity equations<sup>(13)</sup> for momentum, number, and energy. We have verified that the former two are satisfied exactly by the data; the maximum discrepancy in the last decreases with  $\Delta t$  and is about 1% of the average energy content for  $\Delta t = 0.0105$  and

$\tau = 0.105$  (increasing to 5% at  $\tau = 0.419$ ). This is a very strong check on the calculations of both the contents and the transfers, since they are done quite independently. It is also a stronger check on the Verlet trajectories than the usual overall conservation of energy (which is also satisfied, to a few parts in  $10^5$  for  $N = 108$ ). The average longitudinal momentum transfer, which is proportional to the virial pressure, was computed as  $9.53 \pm 0.02$  ( $N = 32$ ) and  $9.48 \pm 0.015$  ( $N = 108$ ) [in units of  $(\epsilon m)^{1/2}$ ]. This should be  $P/\rho kT$ , which is known for the Monte Carlo work<sup>(6)</sup> to be 9.45; agreement is very good.

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