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Calculation of the Mutual Diffusion Coefficient by Equilibrium and Nonequilibrium Molecular Dynamics[1]

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A nonequilibrium molecular dynamics method for the calculation of the mutual diffusion coefficient for a mixture of hard spheres is described. The method is applied to a 50–50 mixture of equidiameter particles having a mass ratio of 0.1 for the two species, at a volume of three times close-packing. By extrapolating the results to the limit of vanishing concentration gradient and infinite system size, we obtain a value in statistical agreement with the result obtained using a Green–Kubo molecular dynamics procedure, which is also described. The nonequilibrium calculation yields a mutual diffusion coefficient which decreases slightly with increasing concentration gradient. The Green–Kubo time-correlation function for mutual diffusion displays a slow decay with time, qualitatively similar to the long-time tail which has been predicted by the hydrodynamic theory of Pomeau.

KEY WORDS: hard spheres; mixtures; molecular dynamics; Monte Carlo; mutual diffusion; time-correlation functions.

1. INTRODUCTION

The study of transport phenomena in fluids from a knowledge of the interaction potential acting between the constituent atoms and molecules has a rich history, dating from the work of Boltzmann [1]. Nonetheless, compared to the situation encountered with the theory of the equilibrium equation of state, the calculation of transport coefficients is far from routine, whether through analytic theory or numerical simulation. The source of these complications is found in the nonanalytic behavior of the

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transport coefficients in the limit of vanishing density [2], leading to difficulties in extending the Boltzmann theory to nonzero density.

A closely related result in the theory of transport processes is the occurrence of the long-time tails of the time correlation functions which enter the Green–Kubo formulation of transport coefficients [2]. In that approach, one writes the transport coefficient μ as

$$\mu = \lim_{t \to \infty} \operatorname{tlim} \mu(t, N) \tag{1}$$

$$\mu(t, N) = c_\mu \int_0^t dt' \, \rho_\mu(t', N) \tag{2}$$

$$\rho_\mu(t, N) = \langle J_\mu(0) \, J_\mu(t) \rangle_N \tag{3}$$

in terms of the time correlation function $\rho_\mu(t, N)$. The latter are given through the equilibrium ensemble averages, $\langle \cdots \rangle_N$, of a microscopic current J_μ which are known functions of the phase $x^N = (r^N, v^N)$ of the system,

$$J_\mu(t) = J_\mu[x^N(t)] \tag{4}$$

where $v^N = (v_1, v_2, \dots, v_N)$ denotes the velocities of the N particles, and $r^N = (r_1, r_2, \dots, r_N)$ the positions. The displayed dependence of the correlation function on N indicates the dependence on the finite size of the system rather than any limitation to a fixed N ensemble. The passage to the thermodynamic limit is indicated by tlim in Eq. (1).

A major difficulty in determining the transport coefficients by the Green–Kubo method arises from the slow $t^{-d/2}$ (for $d = 2$- or 3-dimensional systems) decay of $\rho_\mu(t, N)$ with time for many transport coefficients [3–6], both observed through molecular dynamics experiment and predicted by theory, instead of the exponential decay predicted by the Boltzmann theory. For molecular dynamics calculations of the transport coefficients, this circumstance raises the need to obtain the correlation functions at long times for which $\rho_\mu(t, N)$ is dominated by finite-system effects, at least for times such that hydrodynamic modes have traversed the system. To delay the appearance of these finite-system effects to sufficiently long times can require that rather large systems be studied, say, of the order of 4000 particles.

The alternative to the direct calculation of time-correlation functions at long times and for large systems is the application of theoretical results at these long times. Indeed, the mode-coupling theory has been applied to time correlation functions by Ernst et al. [6], who have computed the dominant long-time contributions to the correlation functions for self-diffusion, shear and bulk viscosity, and thermal conductivity. These results are not, however, immediately useful because the theory does not yield an estimate for the time at which the long-time tail contributions dominate. Thus, one must match the molecular dynamics results to the mode-coupling results in order to complete the calculation of the transport coefficient. The studies of Erpenbeck and Wood for hard-sphere and hard-disk systems [4], in addition to supporting the validity of the mode-coupling results for self-diffusion, also indicate how the theoretical long-time contributions can be merged with the molecular dynamics results.

A number of alternatives to the Green–Kubo calculation have been devised, which are generically referred to as nonequilibrium molecular dynamics [7]. For the present purposes, it is convenient to classify these as either boundary condition methods or constraint methods, even though several techniques fit neither of these categories. The boundary-condition methods are calculations in which the equations of motion of the system contain only the interparticle interactions, just as in equilibrium molecular dynamics. At the boundaries, however, work is performed and heat is extracted from the system, the effect of which is expected to drive the system to a steady-flow state characterized by currents and gradients in the desired quantities from which one can compute the transport coefficient. The boundary conditions are chosen in such a way that the requisite transport property is most simply extracted, a procedure entirely analogous to that used in laboratory experiments.

The constraint techniques are considerably less obvious and potentially of greater power in the study of transport processes. The idea here is to modify the equations of motion via external forces in such a way that the system will approach a steady state in which a current of the desired quantity is achieved and in which gradients in other thermodynamic state variables are absent [8]. Indeed, more recent developments [9] proceed in a completely homogeneous way, with the system containing no gradients. Rather the external forces are used to drive the steady current. One difficulty with this approach arises from the lack of uniqueness of the terms added to the equation of motion, a circumstance which is, at least intuitively, somewhat discomforting.

The simplest of the boundary-condition methods is perhaps a method for self-diffusion [10] in which only the labels attached to the otherwise identical particles are changed in such a way as to maintain a steady self-diffusion current through the system; aside from labeling, the system is in equilibrium and a Green–Kubo calculation and the nonequilibrium calculation can be done in the same molecular dynamics calculation.

The purpose of the present paper is to present a generalization of the self-diffusion method to mutual diffusion by permitting the two different hard-sphere species to differ in mass but not in diameter. The systems under consideration will then be "isotopic" mixtures. In this paper, we describe the method and illustrate its application to a 50–50 mixture of heavy and light hard spheres at a single value of the density. We then compare the resulting mutual diffusion coefficient to the Green–Kubo result, which is also detailed here.

2. SYSTEM AND BOUNDARY CONDITIONS

The system consists of N hard spheres of diameter σ, N_1 particles having mass m_1, and $N_2 = N - N_1$ having mass m_2 contained in a cubic volume V. The system evolves in time under Newton's equations of motion to generate the N-particle trajectory, $x^N(t)$, subject to the following boundary conditions. In the y and z directions, we impose ordinary periodic boundary conditions. In the x direction, however, periodic boundary conditions are modified whenever a particle crosses one of the planes $x = \nu L$, where ν is a signed integer and L is the edge length of the system, $L = V^{\frac{1}{3}}$. If a particle of species 1 with $v_x < 0$ (as well as all its images) crosses such a boundary, then with probability ζ_1 it is relabeled as a particle of species 2 and its velocity is rescaled to conserve energy exactly and to rescale linear momentum approximately. Similarly, a particle of species 2 with $v_x > 0$ which crosses one of the planes is changed to a particle of species 1 with probability ζ_2. The result of these changes will be to build up a concentration gradient, with species 1 concentrating at the left boundary of any cell, $\nu L < x \leqslant (\nu + 1)L$, and species 2 at the right boundary. The details of the velocity modifications will appear elsewhere [11]. It is expected that by fixing the probabilities ζ_1 and ζ_2, the system should approach with time a state of steady diffusion current.

3. OBSERVATIONS AND DATA ANALYSIS

The object of our calculation is, of course, the mutual diffusion coefficient. Macroscopically, if the chemical potential at the position r in the fluid is $\mu(r)$, with gradient $\nabla\mu(r)$, and we denote the diffusion current of species s by $J_s(r)$, then we define the mutual diffusion coefficient D by [12]

$$J_s(r) = -(\rho_s n_s / n k_B T) D \, \nabla \mu_s(r) \tag{5}$$

where we have assumed a steady state and omitted the time as an argument. Here ρ_s and n_s are, respectively, the mass and number densities of species s, n is the total number density, T is the thermodynamic temperature, and k_B is Boltzmann's constant. Because both species have the same hard-sphere diameter, the chemical potential may be written as the sum of an ideal mixing term and a term arising from the hard-sphere repulsion, depending only on the total density and the temperature,

$$\mu_s(n, T, x_1) = k_B T \ln x_s + \hat{\mu}_s(n, T) \tag{6}$$

In our calculations, we assume the system to be isothermal so that

$$|\nabla \mu_s| = (k_B T/x_s)\, \Gamma_s \tag{7}$$

$$\Gamma_s = |\nabla x_s| \tag{8}$$

$$J_s = -\rho_s D \Gamma_s \tag{9}$$

While thermal diffusion will certainly cause our system to have a nonuniform temperature, the expected magnitude of the thermal diffusion coefficient [11], based on the Enskog theory, would predict quite a small deviation from uniformity, in agreement with our observations.

The present calculations consist of the observation of the mass density, mole fraction, and diffusion current at a sequence of times $t_1, t_2, \ldots$ within each of P layers of the system defined by equispaced planes normal to the x axis between 0 and L,

$$\rho_{s/p} = (P/V) \sum_i m_i(t)\, U_l[x_i(t_p)]\, \delta_i^{(s)}(t_p) \tag{10}$$

$$x_{s/p} = n_{s/p} \Big/ \sum_r n_{r/p} \tag{11}$$

$$n_{s/p} = (P/V) \sum_i U_l[x_i(t_p)]\, \delta_i^{(s)}(t_p) \tag{12}$$

$$J_{s/p} = (P/V) \sum_i m_i(t)\, u_i(t_p)\, U_l[x_i(t_p)]\, \delta_i^{(s)}(t_p) \tag{13}$$

$$U_l(x) = A(x - c_l) - A(x - c_{l+1}) \tag{14}$$

where $A(x)$ is the unit step function, $\delta_i^{(s)} = 1$ if particle i is of species s and vanishes otherwise, the c_l are layer coordinates

$$c_l = lL/(P-1), \qquad l = 0, 1, \ldots, P-1 \tag{15}$$

and u_i is the velocity of particle i relative to the center of mass velocity,

$$u_i(t) = v_i(t) - P(t)/M(t) \tag{16}$$

$$P(t) = \sum_i m_i(t)\, v_i(t) \tag{17}$$

$$M(t) = \sum_i m_i(t) \tag{18}$$

It should be noted that the mass of a particle m_i is a function of the time under the current nonequilibrium boundary conditions.

A value of the mutual diffusion coefficient could, of course, be computed for each layer and observation time from Eq. (9) by obtaining an estimate of Γ_s from the mole-fraction profile. In fact, this is not the best way to analyze our data. Instead, we observe at the outset that the mutual diffusion coefficient should have a marked dependence on the density, as can be seen from the Enskog theory result (in the first Sonine polynomial approximation) [13],

$$D_E[1] = \frac{m_1 m_2 n^2}{\rho_1 \rho} - \frac{3}{8n\sigma^2\chi_c}\left[\frac{k_B T(m_1 + m_2)}{2\pi m_1 m_2}\right]^{\frac{1}{2}} \tag{19}$$

in which χ_c is the pair correlation function at contact for the equilibrium state. While the total number density is not found to vary widely in our steady-state profile, the denominator $\rho_1 \rho$ is expected to do so. Therefore we compute values of the diffusion coefficient scaled by $D_E[1]$,

$$\hat{D} = D/D_E[1] \tag{20}$$

in which the values of the densities which enter the latter are obtained from the layer of fluid under consideration and for a particular observation time.

The frequency with which we make observations of the above quantities has considerable influence on the correlations which are found between the sequential observations of any one of them. In the calculations reported here, observations were made at intervals of approximately two mean free times. The resulting values were then coarse-grained over a much longer time interval (ranging from 80 to 1000 such times) so that the resulting set of observation appeared to be serially uncorrelated when subjected to standard statistical tests [14].

While in theory we could determine the reduced diffusion coefficient as a function of density by analyzing individual layers, estimates obtained in that way are not very precise because of the magnitude of the fluctuations. Instead we have averaged our results over a number of layers to obtain an effective mutual diffusion coefficient. Because in the end we are interested in the limit of vanishing composition gradient, the state approached in the extrapolation to this limit is expected to be unique. In practice, we have, for the most part, averaged over either the entire cell or the entire cell except the two boundary layers.

4. RESULTS

The procedure outlined above has been applied for a (initially) 50–50 mixture of hard spheres at a volume of three times close-packed, $V = 3V_0$,

Table I. Parameters and Results for the Nonequilibrium Molecular Dynamics Calculation of the Mutual Diffusion Coefficient[a]

N	ζ_1	ζ_2	N_c	M	N_{obs}	$\hat{D}(N, \Gamma_1)$	Γ_1/σ	x_1
108	1.00	1.00	1.5	120	116	1.02 ± 0.02	0.128 ± 0.002	0.507 ± 0.001
108	0.80	0.80	3.1	160	175	1.05 ± 0.03	0.075 ± 0.001	0.514 ± 0.003
108	0.57	0.57	6.5	1000	59	1.08 ± 0.03	0.042 ± 0.001	0.5283 ± 0.0002
500	1.00	1.00	2.1	80	42	1.05 ± 0.03	0.080 ± 0.001	0.4624 ± 0.0005
500	0.75	0.75	8.0	200	77	1.08 ± 0.03	0.042 ± 0.001	0.5262 ± 0.0001
2048	0.90	1.00	14.1	100	66	1.10 ± 0.02	0.043 ± 0.001	0.534 ± 0.001

[a] N is the number of particles, ζ_1 and ζ_2 are the probabilities for modifying the mass for each type of boundary crossing, N_c is the number of collisions, in millions, for the calculation, M is the number of time steps (two mean free times each) which are coarsed-grained in forming an observation, N_{obs} is the total number of such observations, $\hat{D}$ is the reduced mutual diffusion coefficient, Γ_1 is the magnitude of the mole-fraction gradient, and x_1 is the observed mole-fraction of the heavy species.

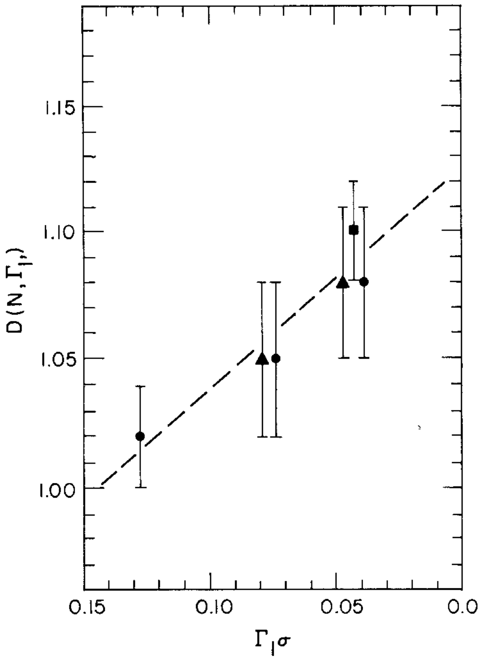

Fig. 1. The mutual diffusion coefficient (in units of the Enskog value) as a function of the mole-fraction gradient for three systems of 108 particles (circles), 500 particles (triangles), and 2048 particles (square). The error bars represent one standard deviation. The three values plotted near $\Gamma_1 = 0.05$ have been separated slightly to perlit the individual error estimates to be distinguished.

where $V_0 = 2^{\frac{1}{2}} N\sigma^3/2$, in which $m_2 = 0.1 m_1$. The set of six calculations which were performed is described in Table I. These comprise three values of the total number of particles and as many as three different values for the mass-change probabilities ζ_1 and ζ_2. The numbers M of observation times coarse-grained in forming the overall averages are tabulated, as are the average values of the mole fraction x_1, its gradient Γ_1, and the reduced mutual diffusion coefficient along with their associated statistical uncertainty (one standard deviation of the mean). The mutual diffusion coefficient is plotted as a function of the reduced mole-fraction gradient in Fig. 1. We observe only a small dependence of $\hat{D}$ on the concentration gradient, decreasing with increasing magnitude of the gradient. The dependence of the results on the number of particles is evidently small. Using linear least squares to extrapolate to vanishing gradient and infinite system size, we obtain the estimate

$$\hat{D} = 1.13 \pm 0.03 \tag{21}$$

in which the uncertainty reflects the range of least-squares results, depending on which terms in $1/N$ and Γ are included in the fit.

5. GREEN–KUBO RESULTS

As a check on the validity of our procedures, we have also evaluated the mutual diffusion coefficient using the Green–Kubo approach. This calculation is based on Eqs. (1)–(4), with [15]

$$\begin{aligned} J_{\mathrm{D}}(t) &= \sum_i m_i u_{xi}(t)\, \delta_i^{(1)} \\ c_{\mathrm{D}} &= \rho n/\rho_1 \rho_2 \rho_1 V \end{aligned} \tag{22}$$

in which the velocity in the center of mass frame of reference is given in Eq. (16). Our calculations are made in the so-called molecular dynamics ensemble of fixed N, V, E, and $P = 0$ using a Monte Carlo-molecular dynamics method which has been detailed elsewhere [10]. The calculations involve Monte Carlo averaging both over a sequence of Q phases $\{x_q{}^N, q = 1, 2, ..., Q\}$ selected by the ordinary Metropolis technique and over time origins defined periodically along the dynamical trajectory generated beginning with each of the Monte Carlo phase points $x_q{}^N$. For the purposes of obtaining a value for the diffusion coefficient, it is convenient to interchange the ensemble average and the time integral in Eqs. (2) and (3), so that we compute

$$D(t, N) = c_{\mathrm{D}} \langle J_{\mathrm{D}}(0)\, G_{\mathrm{D}}(t) \rangle \tag{23}$$

where

$$\begin{aligned} G_{\mathrm{D}}(t) &= \int_0^t dt'\, J_{\mathrm{D}}(t') \\ &= \sum_i m_i\, \Delta x_i(t)\, \delta_i^{(1)} \qquad (24) \\ \Delta r_i(t) &= r_i(t) - r_i(0) \end{aligned}$$

Calculations of $D(t, N)$ as well as the time-correlation function $\rho_{\mathrm{D}}(t)$ have been made for systems of 108, 500, 1372, and 4000 particles. The important parameters of these calculations are given in Table II. The values of the reduced (time-dependent) mutual diffusion coefficient $\hat{D}(t^*, N)$, evaluated at the longest time $t^* = 72t_0$, where t_0 is the mean free time, are plotted against $1/N$ in Fig. 2 and are also given in Table II. These are evidently consistent with a $1/N$ linear extrapolation. A linear least-squares fit yields

$$\hat{D}(t^*) = 1.14 \pm 0.02 \qquad (25)$$

To complete the calculation of D, we require the contribution to the integral, Eq. (1), beyond t^*. The reduced velocity correlation function,

$$\hat{\rho}(s, N) = \{nt_0/V\rho_1\rho_2 D_{\mathrm{E}}[1]\}\, \rho_{\mathrm{D}}(st_0, N) \qquad (26)$$

is plotted in Fig. 3 against $s^{-3/2}$ for values of the reduced time between $s = 8$ and $s = 30$. The mode-coupling theory of Pomeau [16] predicts a

Table II. Parameters and Results for Green–Kubo Calculation of the Mutual Diffusion Coefficient[a]

N	Q	N_c	$\hat{D}(s^*, N)$
108	60	40.4	1.04 ± 0.01
500	100	51.6	1.08 ± 0.02
1372	79	67.0	1.13 ± 0.04
4000	100	102.9	1.18 ± 0.06

[a] N is the number of particles, Q is the number of trajectories, selected by Metropolis Monte Carlo, N_c is the total number of collisions, in millions, for all trajectories, and $\hat{D}(s^*, N)$ is the observed mutual diffusion coefficient obtained from the integral of the Green–Kubo integrand out to a time of 72 mean free times.

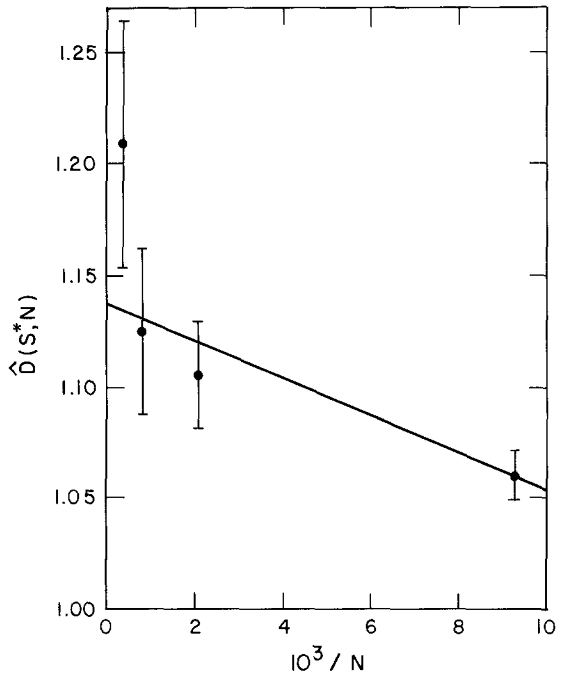

Fig. 2. The mutual diffusion coefficient (in units of the Enskog value) evaluated as the integral of the Green–Kubo time-correlation function to a time of $s^* = 72$ mean free times, as a function of the number, N, of hard spheres in the system.

linear dependence on this form at long times. Beyond about $s = 25$, the statistical uncertainty of the data exceeds the magnitude of the time-correlation function. It is clearly difficult to draw any solid conclusion concerning the long-time behavior. Nonetheless, we can obtain an estimate by assuming a linear $s^{-3/2}$ dependence beyond, say, $s = 22$ and fit our data to obtain an estimate for the long-time tail. This procedure yields a correction to Eq. (25) for long times of $\Delta\hat{D} = 0.05 \pm 0.02$. This is in contrast to the value given using the theoretical coefficient of the long-time tail [16], $\Delta\hat{D} = 0.01$. Our present treatment of the data is unable to resolve this uncertainty. Nonetheless, in view of the strong evidence for the validity of mode-coupling theory in the context of the velocity autocorrelation function [4], we believe the addition of the contribution from the theoretical long-time tail to be entirely reasonable. Thus, we report the Green–Kubo result as

$$\hat{D} = 1.15 \pm 0.02 \tag{27}$$

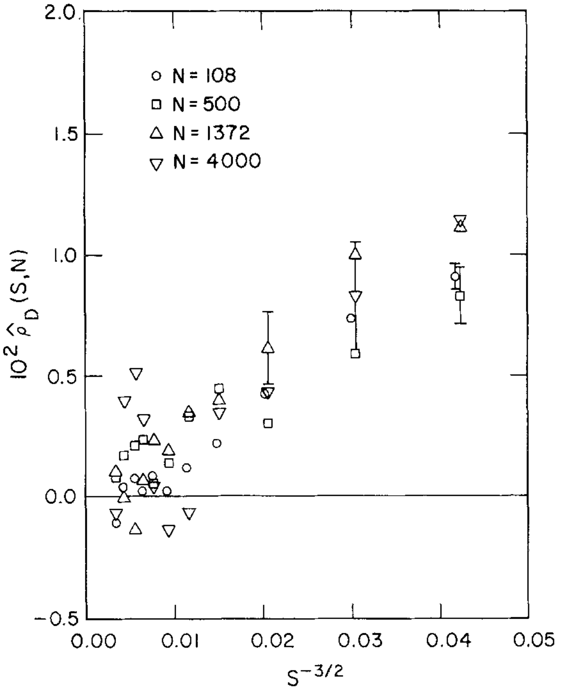

Fig. 3. The reduces time-correlation function for mutual diffusion as a function of the time, *s*, in units of the mean free time, for four different values of the number of particles, *N*. The error bars are one standard deviation and are almost independent of the time.

An independent argument for this result rather than the value 1.19 ± 0.04 suggested by the analysis of the Fig. 3 data must await a more thorough comparison between our data and the theory, perhaps using a finite-N version of the theory to extend the comparison to much shorter times, as discussed in Ref. 4 for the case of the velocity autocorrelation function.

6. DISCUSSION

The apparent agreement between the Green–Kubo and the nonequilibrium molecular dynamics calculations supports the validity of our nonequilibrium method. A number of points are worth stressing.

(i) The fact that the nonequilibrium estimate lies below the Green–Kubo estimate, coupled with the fact that most of the uncertainty in the former estimate is associated with difficulties in taking the limits of large system size and vanishing gradient, is perhaps suggestive of the possibility that contributions to the nonequilibrium estimate analogous to the long-time tail correction to the Green–Kubo values remain hidden in our treatment of the data.

(ii) The observed dependence of the mutual diffusion coefficient on the concentration gradient has not, to our knowledge, been seen experimentally. It would be interesting to know whether such an effect exists in nature.

(iii) The present nonequilibrium method shows no measureable advantage over the Green–Kubo procedure in determining the mutual diffusion coefficient. However, our procedure is expected [9] to be far less "efficient" in producing values for the transport coefficient than the constraint methods, according to proponents of the latter techniques. The case of mutual diffusion may indeed be the optimal choice for a test.

(iv) The question of the validity of the Pomeau theory [16] of the long-time tail has not been seriously addressed in the present work. In view of the large statistical uncertainties in the present data for the time-correlation function at long times, it will evidently require a finite-system version of the theory in order to make the comparison in a time regime where the data have sufficient precision.

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