Long-Time Behavior of the Velocity Autocorrelation Function for a Fluid of Soft Repulsive Particles

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By a molecular-dynamics simulation of a three-dimensional system of 4000 particles, we show that the long-time tail of the velocity autocorrelation function has the form $\alpha_0 t^{-3/2}$, where t is the time and α_0 a coefficient depending on the kinematic viscosity and on the diffusion coefficient.

Alder and Wainwright[1] have shown through molecular-dynamics computations on systems of hard disks and hard spheres that the velocity autocorrelation function (vaf) decreases like $\alpha_0 t^{-d/2}$ when the time t is large compared to the collision time (d is the dimensionality of the system, α_0 is a coefficient dependent upon the density ρ). This behavior has been justified in the limit of small densities by kinetic theory[2] and has been shown to be plausible for a fluid system at all densities on the basis of hydrodynamical arguments.[3] Thus, for three dimensions at large time, the vaf $\langle \vec{V}(0)\cdot\vec{V}(t)\rangle$ should be given by

$$\langle \vec{V}(0)\cdot\vec{V}(t)\rangle = \frac{2k_B T}{\rho m}\frac{1}{[4\pi(D+\nu)t]^{3/2}},$$

where k_B is Boltzmann's constant, T the temperature, m the mass of the particles, D the self-diffusion coefficient, and ν the kinematic viscosity.

However, in molecular-dynamics calculations, the asymptotic behavior $\alpha_0 t^{-3/2}$ can be observed only for times t such that the boundary conditions have no influence on the vaf. More precisely, the time t has to be smaller than some characteristic time $t_0 \sim l/c$, where l is the length of the edge of the cubic box containing the system and c is the sound velocity. Thus, when the number of particles is too small, at any density, l is too small for the asymptotic regime to be reached for $t < t_0$. In the work of Alder and Wainwright[1] on hard spheres, the number of particles is 500 and t_0 is nearly equal to the time when the asymptotic regime starts. The aim of the present study is to calculate the velocity autocorrelation of a fluid system with a number of particles sufficiently large for the asymptotic regime to be reached at a time $t < t_0$. This allows an accurate test of the validity of the above expression for α_0 at high density.

We have computed the vaf for a system of 4000 particles interacting through a potential

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \epsilon \quad \text{for} \quad r \leq 2^{1/6}\sigma,$$

$$= 0 \quad \text{for} \quad r > 2^{1/6}\sigma.$$

The density is $\rho = 0.45$ particles/σ^3 and the temperature $T = 2.17\epsilon/k_B$. At this density and temperature the thermodynamic properties are

$$P/\rho k_B T = 2.72, \quad U_i/Nk_B T = 0.347,$$

$$C_v/k_B = 1.89, \quad (k_B T)^{-1}(\partial P/\partial T) = 5.70,$$

$$(k_B\rho)^{-1}(\partial P/\partial T)_\rho = 2.34,$$

where P is the pressure, U_i the internal energy, and C_v the specific heat at constant volume. These thermodynamical properties are computed either in the molecular-dynamics calculation, or by the perturbation theory[4] which is accurate to within a few percent. The sound velocity is $c = 0.621\sigma/\tau_0$, where τ_0 is the chosen time unit

$$\tau_0 = (m\sigma^2/48\epsilon)^{1/2}.$$

At the density considered, the system is enclosed in a cube whose edge is

$$l = 20.714\sigma,$$

so that $t_0 \sim 33\tau_0$. The movement of the particles is calculated by the algorithm

$$\vec{x}_i(t+h) = \vec{x}_i(t-h) - 2\vec{x}_i(t) + h^2\vec{F}_i(t),$$

$$\vec{v}_i(t+h) = \vec{v}_i(t-h) + 2h\vec{F}_i(t),$$

where $\vec{x}_i(t)$ and $\vec{v}_i(t)$ are the position and velocity of particle i at time t; h is the integration step, $h = 0.032\tau_0$.

The vaf $f(t)$ is obtained at time $t = kh$, where k

TABLE I. Normalized vaf of the two molecular dynamics computations and the weighted average. The time t is divided by the step of the integration h.

t/h			
0	1.0	1.0	1.0
20	0.69170	0.69166	0.69169
40	0.41428	0.41378	0.41410
60	0.25893	0.25834	0.25872
80	0.17202	0.17135	0.17178
100	0.12202	0.12118	0.12172
120	0.09166	0.09070	0.09131
140	0.07162	0.07091	0.07136
160	0.05735	0.05711	0.05726
180	0.04655	0.04663	0.04658
200	0.03845	0.03870	0.03854
220	0.03217	0.03243	0.03226
240	0.02723	0.02711	0.02719
260	0.02305	0.02272	0.02293
280	0.01986	0.01905	0.01957
300	0.01716	0.01654	0.01694
320	0.01504	0.01485	0.01497
340	0.01343	0.01334	0.01340
360	0.01224	0.01227	0.01225
380	0.01102	0.01109	0.01105
400	0.00989	0.00960	0.00979
420	0.00903	0.00829	0.00876
440	0.00815	0.00724	0.00782
460	0.00735	0.00654	0.00706
480	0.00658	0.00605	0.00639
500	0.00599	0.00555	0.00583
520	0.00551	0.00527	0.00542
540	0.00513	0.00494	0.00506
560	0.00469	0.00492	0.00477
580	0.00440	0.00485	0.00656
600	0.00431	0.00454	0.00439
620	0.00421	0.00441	0.00428
640	0.00396	0.00409	0.00401
660	0.00380	0.00399	0.00387
680	0.00382	0.00375	0.00379
700	0.00359	0.00350	0.00356
720	0.00323	0.00356	0.00335
740	0.00312	0.00356	0.00328
760	0.00324	0.00339	0.00329
780	0.00320	0.00340	0.00327

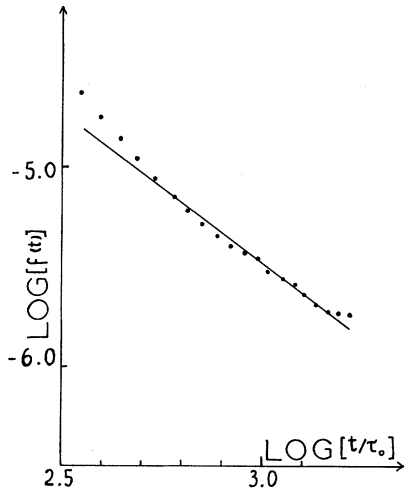

FIG. 1. The log-log plot of the function $f(t)$ for $t > 400h$ (dots). The full line is a straight line with a slope $-\frac{3}{2}$.

is an integer, by the formula

$$f(kh)=\frac{\sum_{l=k_0,k_0+n,\ldots}^{p}\left\{\sum_{i=1}^{N}\vec{v}_i(lh)\cdot\vec{v}_i[(l-k)h]\right\}}{\sum_{l=k_0,k_0+n,\ldots}^{m}\left\{\sum_{i=1}^{N}\vec{v}_i(lh)\cdot\vec{v}_i(lh)\right\}},$$

where p is the total number of integration steps carried out from given initial conditions. For practical reasons, the sum over l is not computed over all integration steps but only for $l=k_0$, $l=k_0+n$, $l=k_0+2n$, $l=k_0+3n,\ldots$ with $n=20$ and $k_0=800$. The maximum value of k is $k_m=780$. The values of p for two calculations done at the same temperature but starting from different initial conditions were $p=18\,600$ and $p=24\,000$.

Last, to avoid any rounding-off error in the calculation, all computations were made using the integer arithmetic of the computer. Each calculation takes about 30 h on a UNIVAC 1110 computer.

The results of the two calculations are given in Table I, together with the weighted average according to the number of integration steps. Figure 1 shows, on a log-log scale, the average vaf. Figure 2 shows the ratio $R(t)$ of the vaf $f(t)$ to a function $\gamma t^{-3/2}$, where γ is chosen so that for $t=620h$ this ratio is 1.

From the numbers of Table I, one can estimate the statistical error on the vaf: The difference between the two calculations is maximum for $k=740$, where it amounts to 14% of the average value of $f(t)$. Between $t=0$ and $t=200h$, this difference is smaller than 1%, between $t=220h$ and

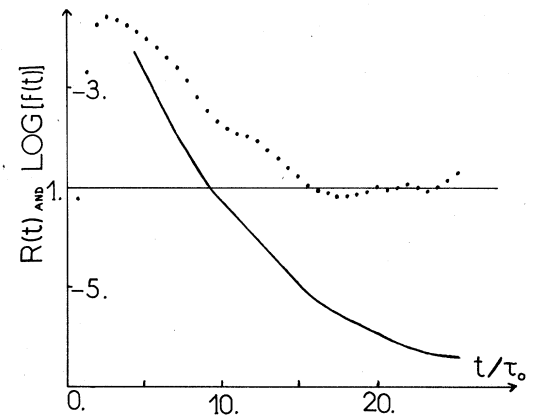

FIG. 2. The ratio $f(t)t^{3/2}/\gamma$ (dots) and the function $\log f(t)$ (full curve) versus t.

$400h$ it is of the order of 2% but sometimes reaches 4%; finally between $400h$ and $780h$ it is roughly 5 or 6%, with the already mentioned exception at $740h$. The average error on $f(t)$, for $t > 400h$, can therefore be estimated to be 7 or 8%. The maximum time for which $f(t)$ is calculated is $t_m \simeq 25\tau_0$. This time is sufficiently smaller than $t_0 \sim 33\tau_0$ for the effect of the boundary conditions to be negligible.

Figure 1 shows the log-log plot of $f(t)$: For $t > 460h$ the plot is nearly linear. This result is confirmed in Fig. 2, where the ratio $R(t) = f(t)/\gamma t^{-3/2}$ fluctuates around 1 for $t > 460h$. The amplitude of the oscillation of $R(t)$ around 1 is never greater than 7%, which is within the error on $f(t)$.

If one assumes that for $t > 460h$, $f(t)$ is of the form $f(t) \sim \alpha t^{-3/2}$ with $\alpha = \alpha_0 m/3k_B T$ one finds for α the value

$$\alpha = (0.377 \pm 0.01)\tau_0^{3/2}$$

[the uncertainty takes into account the statistical uncertainty in $f(t)$]. This value can be compared with the value predicted by Eq. (1).

If one integrates the vaf from $t = 0$ to $t \sim 460h$ (the time at which the asymptotic $t^{-3/2}$ behavior is reached) one gets a diffusion coefficient $D = 0.0764$. If one then calculates the contribution due to the long-time tail of the vaf, with the value of α given above, one obtains 0.0088, yielding a total D of 0.0852. The contribution of the long-time tail between $t = 460h$ and $t = 780h$ is 0.0020.

The calculation of the kinematic viscosity has been made by one of us by simulation of a Couette flow[5] through molecular dynamics; the result is $\nu = 0.143 \pm 0.03$. The corresponding value for α is $(0.31 \pm 0.07)\tau_0^{3/2}$. The uncertainty comes mainly from the uncertainty in ν; the uncertainty in D is less than 1%. One sees, therefore, that the transport coefficients obtained by molecular dynamics are compatible with Eq. (1). At this degree of accuracy, there is no need to introduce "bare" transport coefficients.[6]

Our calculation shows that the asymptotic regime is reached after a relatively short time. Since the interparticle potential is purely repulsive and of finite range, one can define a collision time using the equivalent hard-sphere radius of perturbation theory.[4] At the density and temperature considered, this collision time is $\tau_{col} = 0.797\tau_0 = 25.53h$. The asymptotic regime is therefore reached after approximately 18 collisions.

Note that the accuracy of our calculation does not enable us to test the predictions concerning the corrections[7] to the main term $\alpha t^{-3/2}$. The coefficient in front of the $t^{-7/4}$ term is indeed a hundred times smaller than α when it is computed using the equivalent hard-sphere radius and the Enskog formulas for the transport coefficients.

For times smaller than $400h$, when the asymptotic regime is not yet reached, the present results are identical to those already obtained[8] at similar density and temperature. In this temperature range, there are two relaxation regimes for the vaf, one quasi-Gaussian, at small times $(0 < t < 200h)$, the other quasi-exponential at times $200h < t < 440h$. This can be seen in Fig. 2. This behavior can be represented in terms of memory function as in Ref. 8.

A last remark concerns the possibility of experimentally observing the asymptotic regime, for example, in argon. The only possibility seems to be to use neutron diffraction measurements of the incoherent dynamic structure factor $S_i(k,\omega)$. One knows that

$$\tilde{f}(\omega) = \lim_{k \to 0} \frac{m\omega^2 S_i(k,\omega)}{k_B T k^2},$$

where $\tilde{f}(\omega)$ is the Fourier transform of $f(t)$ and $\vec{k}$ is the wave vector, and one expects that

$$\tilde{f}(\omega) \sim b - a\alpha\sqrt{\omega} + \ldots,$$

where a, b are some constants. In our calculation, such a behavior is reached for $\omega < 0.02\tau_0^{-1}$. On the other hand, the analysis made in Ref. 8 shows that the amplitude $c_i(k,t)$ of the current autocorrelation function, whose Fourier transform is $\omega^2 S_i(k,\omega)$, decreases very rapidly for large times $(t > 200h)$ when k increases; it is

therefore difficult to make the $k = 0$ extrapolation in Eq. (2) when $\omega \to 0$.

This molecular-dynamics calculation shows that the vaf of a dense gas at a near-critical temperature behaves asymptotically like $\alpha t^{-3/2}$; the value of the coefficient α can be deduced from the transport coefficients ν and D. These results confirm those obtained by Alder and Wainwright[1] and by Wood[9] for systems of 500 and 4000 hard spheres.

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Photographs of Quantized Vortex Lines in Rotating He II*

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The spatial positions of discrete quantized vortex lines in rotating superfluid helium have been directly visualized by a photographic technique. The positions of the lines in the apparatus do not form a regular array.

The unique properties of He II have been associated with the existence of a macroscopic wave function which determines the behavior of the superfluid component. From this idea Onsager[1] and Feynman[2] predicted that He II should exhibit vorticity with circulation quantized in units of h/m, where h is Planck's constant and m is the mass of the helium atom. For almost two decades physicists have been exploring theoretically and experimentally the phenomena associated with these vortices.[3] A wealth of convincing information is available which supports the existence of vortices, the most direct experiments being those which proved that circulation in He II is quantized[4,5] and that He II comes into rotation in a series of quantum steps.[6] There has still been one experiment which has enticed workers for some time: actually to make directly visible the discrete vortex lines in the rotating He II. (An analogous experiment has been done to visualize fluxoids in a superconductor.[7]) This Letter describes the first successful experiment which records the positions of the vortex lines in helium. We point out that according to current ideas the vortex core is a node in the macroscopic wave function. This is one of the only measurements we know which directly measure the positions of the nodes of a wave function.

The method we employ is conceptually simple.[8] Vortex lines should appear in a container of He II rotating at angular velocity ω, with a predicted density[2] of $2\omega m/h$ lines/cm^2. Electrons formed near a radioactive source are injected into the rotating He II. The electrons form bubbles (radius ~ 16 Å) which become trapped on vortex lines in a Bernoulli trapping potential.[9] The lines are charged for about 10 sec, after which an axial electric field is applied which pulls the ions through the liquid meniscus. Once free of the liquid, the electrons are accelerated and impinge on a phosphor screen where they produce a flash of light, thus marking the position of the line where it meets the free surface.

There are numerous complications which conspire to defeat the simplicity of this method. First of all, the experiment must be done at temperatures below 0.6 K so that the helium vapor pressure is low enough to allow the use of elec-