CURRENT AND SPIN DENSITY CORRELATION FUNCTIONS FOR COMPUTER NITROGEN

M.W. EVANS
Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE, UK

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Current and spin density correlation functions are simulated for computer nitrogen using the algorithm of Tildesley and Streett. The functions are oscillatory and non-exponential even for the lowest values of momentum transfer k. A semi-empirical interpretation on the basis of a three-variable Mori approximant is attempted.

1. Introduction

The relation between molecular and hydrodynamic theories of the fluid state is one which will continue to be analytically intractable without the aid of computer simulation techniques. These help to define the overall form of collective correlation functions such as that of the longitudinal and transverse current and spin densities. In a simulation these may be built up from information on individual molecules represented by a potential of chosen form (e.g. an atom–atom Lennard-Jones as used here for nitrogen) and then compared with those usually employed in the hydrodynamic equations of mass, momentum, and energy conservation leading to the linearized Navier–Stokes equation.

In this short communication we present some preliminary results on the simulation of current and spin density correlation functions for N_2 in the liquid and glassy states starting from the atom–atom potential and Newton's equations for individual molecular motions. The results are discussed in terms of generalised hydrodynamic theory as first propounded by Zwanzig et al. [1] for computer argon. This is a theory which is useful also on the molecular scale so that molecular and hydrodynamic theories may be developed in a parallel fashion within the same broad context.

2. Computation and theoretical background

Computations were made of the total spin and current density correlation functions using an ensemble of 256 N_2 molecules interacting atom–atom-wise as defined in the algorithm of Tildesley and Streett [2]. Both the longitudinal and transverse current density correlation functions are expected to be purely exponential decays on the basis of classical hydrodynamic theory, and so is the transverse spin density correlation function. These are defined as follows:

$$C(\boldsymbol{k}, t) = (1/T) \int_0^T J^*(\boldsymbol{k}, s) J(\boldsymbol{k}, s + t) \mathrm{d}s \,, \qquad (1)$$

where the wave-vector $\boldsymbol{k}$ stands for $\boldsymbol{k}_\perp$ or $\boldsymbol{k}_\parallel$, T is the total time of simulation. We have:

$$J(\boldsymbol{k}, t) = N^{-1/2} \sum_\alpha \{ \boldsymbol{p}^{\alpha,1}(t) \exp [\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}^{\alpha,1}(t)] + \boldsymbol{p}^{\alpha,2}(t) \exp [\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}^{\alpha,2}(t)] \} \,, \qquad (2)$$

where $\boldsymbol{p}^{\alpha,1}(t)$ is the momentum of the first atom on the αth molecule, $\boldsymbol{p}^{\alpha,2}(t)$ that of the second atom. $\boldsymbol{r}^{\alpha,1}(t)$ is the position vector of the first atom and $\boldsymbol{r}^{\alpha,2}(t)$ that of the second. In our simulation $N = 256$.

The spin density correlation functions (longitudinal and transverse) are evaluated similarly. To check on the reliability of the statistics in the simulation of these collective correlation functions, the cross-correlation functions of velocity and of force were evaluated using 1600 time steps in segments of 20 minutes on the CDC 7600. Since the algorithm conserves the total linear momentum ($\Sigma_i \boldsymbol{p}_j = \boldsymbol{0}$, ensuring equal action and reaction), then the normalised a.c.f. and c.c.f. of velocity and force should decay identically [3]. This is because:

$$\boldsymbol{v}_j(0) \cdot \sum_{k \neq j} \boldsymbol{v}_k(t) = \boldsymbol{v}_j \cdot \left(\sum_{k=1}^{N} \boldsymbol{v}_k(t) - \boldsymbol{v}_j(t) \right)$$

$$= -\boldsymbol{v}_j(0) \cdot \boldsymbol{v}_j(t) , \qquad (3)$$

since $\Sigma_{k=1}^{N} \boldsymbol{v}_k(t) = \boldsymbol{0}$.

As fig. 1 shows, the cross-correlation function and autocorrelation function of velocity decay similarly, an indication that our statistics are satisfactory up to a real time of 1 ps. All the hydrodynamic functions were evaluated using 1600 time steps of 5×10^{-15} s after rejecting the first 200.

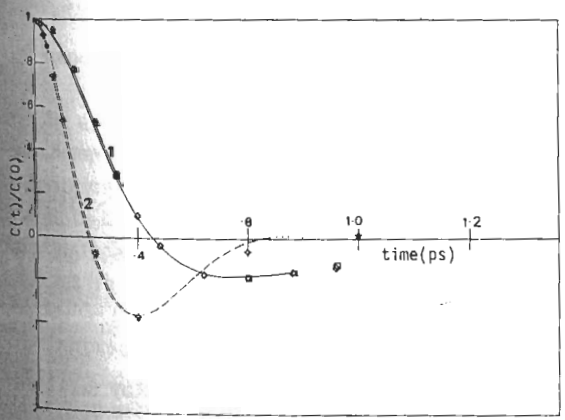

Fig. 1. (1) Autocorrelation function of velocity for N_2 in the liquid state at a reduced number density (p^*) of 0.643, reduced temperature (T^*) of 2.32. ◇, cross-correlation function of velocity, 1000 time steps; □, cross-correlation function of velocity, 1600 time steps. (2) Autocorrelation function of force for N_2 in the same liquid state. ○, cross-correlation function 1600 time steps; ◇, cross-correlation function 1000 time steps.

3. Results and discussion

In fig. 2 are illustrated some $C_{\parallel}(\boldsymbol{k}, t)$ for large and intermediate values of momentum transfer (wave vector) $\boldsymbol{k}$. It is seen that in the N_2 fluid and glass, $C_{\parallel}(\boldsymbol{k}, t)$ are oscillatory with pronounced negative regions as $\boldsymbol{k}$ increases even with $|\boldsymbol{k}| = 0.1$ (in reduced units of $1/\sigma$, where σ is the Lennard-Jones parameter for N_2) the correlation function is far from exponential, as is the assumption of classical Navier–Stokes equations. Our calculations of the transverse current correlation function indicate the same results, as do those for the spin density, and the cross-correlation between transverse spin and current densities.

It is clear therefore that a generalised hydrodynamic formalism is needed to account for the correlation functions simulated in this paper. The form suggested by Ailawadi et al. [1] is:

$$\frac{\partial C_{\parallel}(\boldsymbol{k}, t)}{\partial t} = -\int_0^t K_I(\boldsymbol{k}, t - t') C_{\parallel}(\boldsymbol{k}, t') \, \mathrm{d}t' , \qquad (4)$$

where the memory function $K_I(\boldsymbol{k}, t)$ may be expressed as the sum:

$$K_I(\boldsymbol{k}, t) = k^2 \left[(kT/m) S(\boldsymbol{k}) + \phi_{\parallel}(\boldsymbol{k}, t) \right] . \qquad (5)$$

Here $S(\boldsymbol{k})$ is the equilibrium structure factor determined by a $\boldsymbol{k}$ dependent compressibility, and $\phi_{\parallel}(t)$ is an after-effect, or memory function describing the delayed response of the longitudinal part of the stress tensor to a change in the rate of shear.

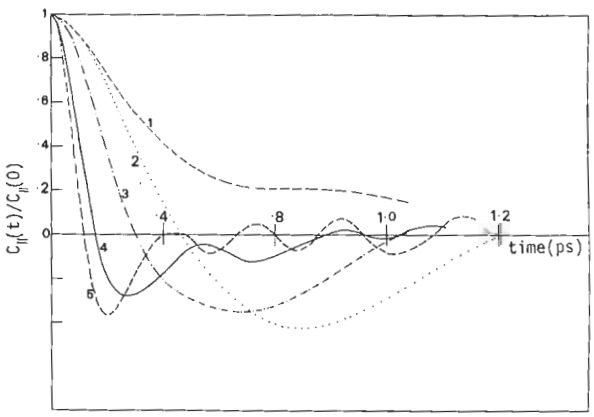

Fig. 2. Longitudinal current density correlation functions for different values of momentum transfer $\boldsymbol{k}$ (in reduced units of σ); (1) $|\boldsymbol{k}|^2 = 0.3$; (2) 3; (3) 15; (4) 45; (5) 60.

We propose here to develop eq. (4) into a Mori continued fraction and in order to maintain compatibility between macroscopic and microscopic levels the series of equations in the Mori expansion of (4) may be truncated at the three variable level already widely used in molecular theories of itinerant oscillation.

Therefore in Laplace transform space (p):

$$\frac{\tilde{C}_{\parallel}(k,p)}{\tilde{C}_{\parallel}(k,0)} = \left[p + \frac{K_l^{(0)}(k,0)}{p + \dfrac{K_l^{(1)}(k,0)}{p+\gamma(k)}} \right]^{-1} \qquad (6)$$

Here $K_l^{(0)}(k,0)$ and $K_l^{(1)}(k,0)$ are the first and second memory functions of $\tilde{C}_{\parallel}(k,p)$ at $t=0$. $\gamma(k)$ is defined by

$$K_l^{(1)}(k,t) = K_l^{(1)}(k,0) \exp\,[-\gamma(k)t]\,. \qquad (7)$$

Of course eq. (5) is empirical in the sense that three parameters are unknown: $K_l^0(k,0)$, $K_l^1(k,0)$ and $\gamma(k)$ and have to be fixed by least mean square iteration to the simulated $C_{\parallel}(k,t)$. However, dependence on $|k|$ may be extracted as illustrated in fig. 3 of ref. [1].

The transverse current density correlation function and the spin density correlation functions oscillate about the time axes in the same way as the above, representative curves being drawn in figs. 2 and 3. The transverse spin density correlation function may not be derived in any other fashion than by computer simulation, since neutron scattering is insensitive in this context. It is obvious that the coupling between transverse spin and current density will be complicated in fluids of more pronounced molecular shape anisotropy than N_2, and the limit of analytical tractability will be reached very quickly in dealing with this rotation/translation problem. This leaves only computer simulation as a practical means of investigation given a suitable intermolecular potential and improved numerical methods.

It would be particularly useful in further work to solve numerically the equations of motion for a given molecular model, such as the itinerant oscillator [5], and then to determine directly whether the current and spin density correlation functions are describable by the same type of Mori approximant as their molecular counterparts. This type of simulation would then be effectively a method of evaluating hydrodynamic functions from a specific molecular model of, say, a brownian motion plus resonance type [4].

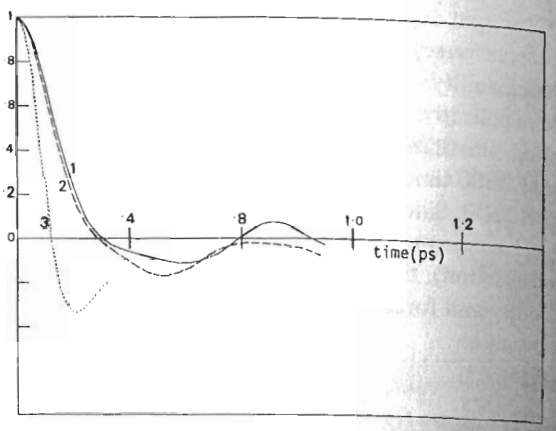

Fig. 3. (1) Longitudinal spin density correlation function, N_2, $p^* = 0.643$, $T^* = 2.32$, $|k|^2 = 45$. (2) Transverse spin density correlation function, N_2, $p^* = 0.643$, $T^* = 2.32$, $|k|^2 = 30$. (3) Longitudinal current density correlation function, N_2, $|k|^2 = 60$. N_2 in the glassy state at $p^* = 0.800$, $T^* = 2.30$.

Acknowledgement

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