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LETTER TO THE EDITOR

The velocity autocorrelation function of an overdamped Brownian system with hard-core interaction

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Abstract. The velocity autocorrelation function is calculated exactly for a system of Brownian particles interacting through hard-core potentials to lowest order in the volume concentration on the basis of the Smoluchowski equation.

A quantity of basic interest in the dynamics of a particle interacting with many other particles in a liquid-like system is the velocity autocorrelation function (VAF). It is closely connected to other important quantities such as the mean square displacement and the self-diffusion coefficient of a tagged particle. Of particular interest is the long-time behaviour of the VAF after Alder and Wainwright (1967) discovered by means of computer experiments the algebraic $t^{-3/2}$ tail for hard-core fluids (in three dimensions). This phenomenon has since been investigated in great detail and applies to all fluids with short-ranged interactions (Pomeau and Résibois 1975). Only in fluids in which the particles interact through Coulomb potentials are the long-time tails of a different type (Baus and Hansen 1980).

In this paper we investigate the VAF for a particular overdamped Brownian system. In recent years there has been great interest both experimentally and theoretically in understanding the dynamical properties of interacting large spherical particles immersed in a solvent (Pusey and Tough 1981). For many purposes the dynamical properties of such systems can well be described on the basis of the N-particle Smoluchowski equation. We calculate the VAF for a system of macroparticles interacting only through their hard cores on this basis exactly to first order in the volume concentration.

Let $\boldsymbol{r}_1(t)$ be the position of the tagged particle at time t. Then

$$c_1(\boldsymbol{k}, t) = \exp[-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}_1(t)] \tag{1}$$

is the contribution of the tagged particle to the total concentration fluctuation of wavevector $\boldsymbol{k}$. From (1) one finds for the velocity $\boldsymbol{v}_1(t) = \dot{\boldsymbol{r}}_1(t)$

$$\boldsymbol{k} \cdot \boldsymbol{v}_1(t) = \mathrm{i}\partial c_1(\boldsymbol{k}, t)/\partial t + \mathrm{O}(k^2). \tag{2}$$

From its definition

$$Z(t-t') = \tfrac{1}{3}\langle \boldsymbol{v}_1(t) \cdot \boldsymbol{v}_1(t')\rangle \tag{3}$$

the VAF can be rewritten using (2) and the isotropy of the system

$$Z(t-t') = \lim_{k\to 0} \frac{\partial^2}{\partial t \partial t'} \frac{1}{k^2} \langle c_1(\mathbf{k}, t) c_1(-\mathbf{k}, t')\rangle$$
$$= -\lim_{k\to 0} \frac{\partial^2}{\partial t^2} \frac{1}{k^2} \langle c_1(\mathbf{k}, t)\, c_1(-\mathbf{k}, t')\rangle. \tag{4}$$

The brackets $\langle\ldots\rangle$ denote an equilibrium expectation value. Equation (4) can finally be expressed as an integral in configuration space

$$Z(t-t') = -\lim_{k\to 0} \frac{\partial^2}{\partial t^2} \frac{1}{k^2} \int \mathrm{d}\{\mathbf{r}_i\} \int \mathrm{d}\{\mathbf{r}_i^0\} \exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r}_1)\, P_N(\{\mathbf{r}_i\}, t|\{\mathbf{r}_i^0\}, t')$$
$$\times \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r}_1^0)\rho_{\mathrm{eq}}(\{\mathbf{r}_i^0\}). \tag{5}$$

Here, $P_N(\{\mathbf{r}_i\}, t|\{\mathbf{r}_i^0\}, t')$ is the probability of finding the system in the configuration $\{\mathbf{r}_i\}$ at time t if it had the configuration $\{\mathbf{r}_i^0\}$ at time t', and ρ_{eq} denotes the equilibrium distribution function.

If one takes the Laplace transform

$$\tilde{Z}(z) \equiv \mathscr{L}\{Z(t)\} = \int_0^\infty \mathrm{d}t \exp(-zt) Z(t) \tag{6}$$

of equation (5) one has to observe that the RHS of equation (3) is symmetric in t and t' so that the time derivative of P_N at $t=t'$ vanishes. Therefore

$$\tilde{Z}(z) = -\lim_{k\to 0} \frac{1}{k^2} \int \mathrm{d}\{\mathbf{r}_i\} \int \mathrm{d}\{\mathbf{r}_i^0\} \exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r}_1)[z^2\mathscr{L}\{P_N\} - zP_N(t=t')]$$
$$\times \exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r}_1^0)\rho_{\mathrm{eq}}(\{\mathbf{r}_i^0\}). \tag{7}$$

For the overdamped Brownian system under consideration the conditional probability P_N satisfies the generalised Smoluchowski equation (GSE) (Deutch and Oppenheim 1971, Murphy and Aguirre 1972)

$$(\partial/\partial t - \hat{\Omega}_N) P_N(\{\mathbf{r}_i\}, t|\{\mathbf{r}_i^0\}, t') = 0 \qquad \text{for } t \geqslant t'. \tag{8}$$

It is now sufficient to restrict oneself to $t > t'$ because of the Laplace transform. In (8) $\hat{\Omega}_N$ is the Smoluchowski operator

$$\hat{\Omega}_N = D_0 \sum_{i=1}^N \frac{\partial}{\partial \mathbf{r}_i}\left(\frac{\partial}{\partial \mathbf{r}_i} + \beta \frac{\partial U_N(\{\mathbf{r}_i\})}{\partial \mathbf{r}_i}\right) \tag{9}$$

where we have neglected the hydrodynamic interaction and where D_0 denotes the diffusion constant of a free particle. Further, $U_N(\{\mathbf{r}_i\})$ is the N-particle interaction potential of the Brownian particles and $\beta = (k_B T)^{-1}$.

The formal solution of (8) is

$$P_N(\{\mathbf{r}_i\}, t|\{\mathbf{r}_i^0\}, t') = \exp[\hat{\Omega}_N(t-t')] \prod_i \delta(\mathbf{r}_i - \mathbf{r}_i^0). \tag{10}$$

The equilibrium distribution $\rho_{\mathrm{eq}}(\{\mathbf{r}_i\})$ is the time-independent solution of (8)

$$\rho_{\mathrm{eq}}(\{\mathbf{r}_i\}) = Z_{\mathrm{eq}}^{-1} \exp[-\beta U_N(\{\mathbf{r}_i\})] \tag{11}$$

where Z_{eq} is the normalisation.

Using (10) in (7)

$$\tilde{Z}(z)=\lim_{k\to 0}\frac{z}{k^2}\left\{1-z\int d\{r_i\}\exp(-ik\cdot r_1)(z-\hat{\Omega}_N)^{-1}\exp(ik\cdot r_1)\,\rho_{eq}(\{r_i\})\right\}. \tag{12}$$

Employing the operator identity

$$(z-\hat{\Omega}_N)^{-1}=\frac{1}{z}[1+\hat{\Omega}_N(z-\hat{\Omega}_N)^{-1}]=\frac{1}{z}\left(1+\frac{1}{z}\hat{\Omega}_N+\frac{1}{z}\hat{\Omega}_N(z-\hat{\Omega}_N)^{-1}\hat{\Omega}_N\right) \tag{13}$$

in (12), performing some partial integrations where the explicit expression (9) of $\hat{\Omega}_N$ is used, the limit $k\to 0$ can be taken with the result

$$\tilde{Z}(z)=D_0(1-D_0\beta^2\tilde{\phi}(z)). \tag{14}$$

Here, $\tilde{\phi}(z)$ is the Laplace transform of the correlation function of the force exerted on the tagged particle by the other Brownian particles

$$\tilde{\phi}(z)=\tfrac{1}{3}\int d\{r_i\}\left(-\frac{\partial U_N(\{r_i\})}{\partial r_1}\right)(z-\hat{\Omega}_N)^{-1}\left(-\frac{\partial U_N(\{r_i\})}{\partial r_1}\right)\rho_{eq}(\{r_i\}). \tag{15}$$

We now specify the interaction between the particles to the hard-core potential

$$U_N(\{r_i\})=\tfrac{1}{2}\sum_{i,j=1}^{N}{}' U(r_{ij}),$$

$$U(r_{ij})=\begin{cases}\infty & \text{for } |r_{ij}|<d\\ 0 & \text{for } |r_{ij}|>d.\end{cases} \tag{16}$$

The prime on the summation denotes $i\neq j$. The diameter of a Brownian particle is d and $r_{ij}=r_i-r_j$. From the radial distribution function

$$g(r_{ij})=\exp[-\beta U(r_{ij})]=\theta(r_{ij}-d) \tag{17}$$

the force on the tagged particle can formally be expressed as

$$-\frac{\partial U_N(\{r_i\})}{\partial r_1}=\beta^{-1}\frac{\partial}{\partial r_1}\frac{1}{2}\sum_{i,j}{}'\ln\theta(r_{ij}-d)=\beta^{-1}\sum_{i=2}^{N}\frac{\partial}{\partial r_{1i}}\ln\theta(r_{1i}-d). \tag{18}$$

Restricting our further investigation to effects of lowest order in the concentration of macroparticles, the force correlation function $\tilde{\phi}(z)$ is given by the sum of two-particle contributions. Because of the statistical equivalence of the particles one obtains from (15) and (18)

$$\tilde{\phi}(z)=\frac{1}{3}\beta^{-2}\left(\frac{N}{V}\right)\int d^3r_{12}\left(\frac{\partial}{\partial r_{12}}\ln\theta(r_{12}-d)\right)\cdot(z-\hat{\Omega}^{r}_{12})^{-1}\left(\frac{\partial}{\partial r_{12}}\ln\theta(r_{12}-d)\right)\theta(r_{12}-d) \tag{19}$$

where $\hat{\Omega}^{r}_{12}$ is the diffusion operator, which corresponds to (9), and describes the relative motion of the two-particle cluster

$$\hat{\Omega}^{r}_{12}=2D_0\frac{\partial}{\partial r_{12}}\cdot\left(\frac{\partial}{\partial r_{12}}+\beta\frac{\partial U(r_{12})}{\partial r_{12}}\right). \tag{20}$$

If $\tilde{\rho}_2(r_{12},z|r^0_{12})$ denotes the Laplace transformed formal solution of the corresponding two-particle diffusion equation

$$\tilde{\rho}_2(\boldsymbol{r}_{12}, z|\boldsymbol{r}_{12}^0) = (z - \hat{\Omega}_{12}^r)^{-1}\delta(\boldsymbol{r}_{12} - \boldsymbol{r}_{12}^0)\theta(r_{12}^0 - d) \tag{21}$$

equation (19) can be rewritten as

$$\tilde{\phi}(z) = \tfrac{1}{3}\beta^{-2}(N/V)\int \mathrm{d}^3 r_{12}\int \mathrm{d}^3 r_{12}^0 \times\left(\frac{\partial}{\partial \boldsymbol{r}_{12}}\ln\theta(r_{12}-d)\right)\tilde{\rho}_2(\boldsymbol{r}_{12}, z|\boldsymbol{r}_{12}^0)\left(\frac{\partial}{\partial \boldsymbol{r}_{12}^0}\ln\theta(r_{12}^0-d)\right). \tag{22}$$

The two-particle diffusion equation can be solved exactly (Hanna *et al* 1981); the result is

$$\tilde{\rho}_2(\boldsymbol{r}_{12}, z|\boldsymbol{r}_{12}^0) = \theta(r_{12}-d)\sum_{l=0}^{\infty}\sum_{m=-l}^{+l} Y_l^m(\Omega)Y_l^m(\Omega^0)^* \times\frac{2}{\pi}\int_0^\infty \mathrm{d}q\, q^2 \frac{j_l(qr_0)}{z+2D_0q^2}\left[j_l(qr) - \left(\frac{2D_0}{z}\right)^{1/2} qj_l'(qd)\frac{k_l[r(z/2D_0)^{1/2}]}{k_l'[r(z/2D_0)^{1/2}]}\right]. \tag{23}$$

Here, $Y_l^m(\Omega)$ are spherical harmonics, $j_l(x)$ denotes spherical Bessel functions, $k_l(x)$ are modified spherical Bessel functions of the third kind and $j_l'(x)$ and $k_l'(x)$ are their derivatives. Performing the integrations with respect to $\boldsymbol{r}_{12}$ and $\boldsymbol{r}_{12}^0$ in (22) (for details see Hanna *et al* 1981), the force correlation function is

$$\tilde{\phi}(z) = \frac{16\eta}{\pi D_0\beta^2}\int_0^\infty \mathrm{d}x\frac{x^2}{x^2+zd^2/(2D_0)} \times\left[j_1^2(x) - xj_1(x)j_1'(x)\left(\frac{2D_0}{zd^2}\right)^{1/2}\frac{k_1[d(z/2D_0)^{1/2}]}{k_1'[d(z/2D_0)^{1/2}]}\right], \tag{24}$$

where $\eta = (4\pi/3)(d/2)^3(N/V)$ denotes the volume concentration. The Laplace back-transform of (24) is

$$\phi(t) = \frac{16\eta}{\pi d^2\beta^2}\int_0^\infty \mathrm{d}x\left(1 - \frac{4}{x^4+4}\right)\exp(-2D_0tx^2/d^2). \tag{25}$$

The remaining integral can be expressed either by Lommel functions (Gradstein and Ryzhik 1965) or by Fresnel integrals (Abramowitz and Stegun 1970). Choosing the latter representation,

$$\phi(t) = \frac{16\eta}{\pi d^2\beta^2}\left[\left(\frac{\pi}{2\tau}\right)^{1/2} - \pi[\cos\tau\,(\tfrac{1}{2} - S([2\tau/\pi]^{1/2})) - \sin\tau(\tfrac{1}{2} - C([2\tau/\pi]^{1/2}))]\right]. \tag{26}$$

Here, $\tau = 4D_0t/d^2$ is a reduced time; $d^2/(4D_0)$ is the time which a free particle needs to diffuse a distance equal to its radius. $S(x)$ and $C(x)$ in (26) denote Fresnel integrals.

Figure 1 displays the result for the force autocorrelation function as a function of τ. From (26), using the asymptotic expansions, $\phi(t)$ behaves for large t as

$$\phi(t) \xrightarrow[t\to\infty]{} \frac{12\eta}{(2\pi)^{1/2}d^2\beta^2}\left(\frac{4D_0}{d^2}\right)^{-5/2} t^{-5/2}. \tag{27}$$

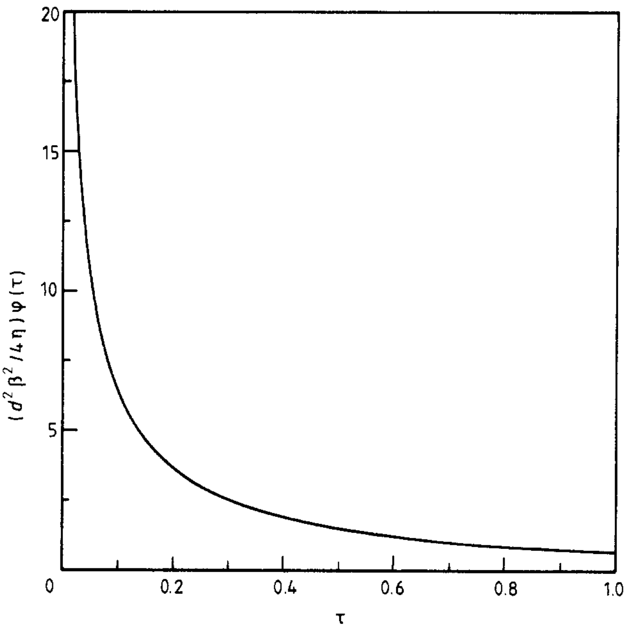

Figure 1. Reduced force autocorrelation function $(d^2\beta^2/4\eta)\phi(t)$ as a function of the reduced time $\tau=(4D_0/d^2)t$.

For short times

$$\phi(t)=\frac{16\eta}{(2\pi)^{1/2}d^2\beta^2}\left(\frac{4D_0}{d^2}\right)^{-1/2}t^{-1/2}+O(t^0). \tag{28}$$

From $\phi(t)$ the VAF can be obtained using (14). The VAF consists of a δ function at $t=0$, followed by an entirely negative contribution which is monotonic. This qualitative form of the VAF was suggested earlier by Pusey (1978) for a system of highly charged polystyrene particles and can be obtained from a mode–mode coupling theory which was developed to describe such systems (Hess and Klein 1981).

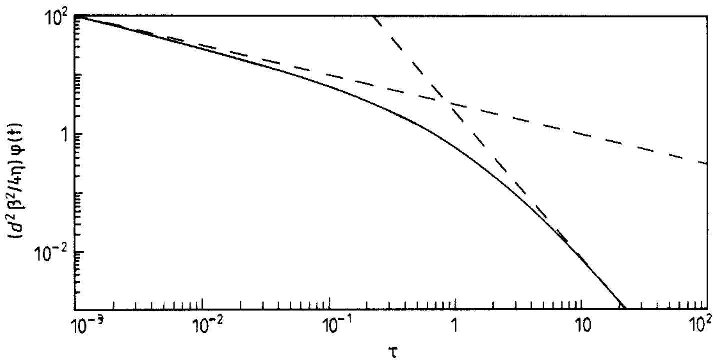

Figure 2. Double-logarithmic plot of the reduced force autocorrelation function (same as figure 1) together with the asymptotic short- and long-time behaviour.

Whereas the VAF of a hard-core fluid had a $t^{-3/2}$ long-time tail, we find for the overdamped Brownian hard-core system $Z(t) \sim t^{-5/2}$ at large t. The same result was obtained earlier for other Brownian systems (Jacobs and Harris 1977, Hess and Klein 1981, Jones and Burfield 1981). This difference is due to the fact that the $t^{-3/2}$ tail has its origin in momentum relaxations. In the overdamped Brownian system the momentum relaxation is much faster than spatial diffusion. This is just the reason why the Smoluchowski equation is under many circumstances a satisfactory basis for the description of overdamped Brownian systems. Therefore, the momentum relaxation tail is hidden in the $\delta(t)$ term in our result for the VAF.

Finally, it should be noted that (26) is proportional to the volume concentration η; for non-interacting Brownian particles this term will vanish and the well known $t^{-3/2}$ tail (Boon and Bouiller 1976, Pusey 1981) will survive. The theoretical description of this situation is however beyond the Smoluchowski equation.

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