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Probability density functions for the translational itinerant oscillator

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The translational itinerant oscillator model for molecular motion in fluids is developed in terms of two phenomenological parameters. These are: (*a*) the retarding frictional force acting on a rigid cage which undergoes translational Brownian motion, and (*b*) the angular frequency of oscillation of a particle hamonically bound within the cage. The equations of motion contain fewer parameters than those of Damle *et al.* [6] and may be solved using Laplace transforms. The underlying probability density functions in phase and configuration space may then be calculated.

1. Introduction

The autocorrelation functions (a.c.f.'s), observable by means of far infra-red/microwave spectroscopy and by depolarized Rayleigh scattering [1], have been calculated recently [2, 3] using a rotational version of the itinerant oscillator model for molecular motion in fluids. In this paper we develop a translational counterpart for fluctuations in space. The essential idea embodied in the model is that an atom or molecule may vibrate about an equilibrium position (corresponding to the mean centre of mass coordinate) determined by its cage of nearest neighbours, which *itself* executes translational brownian motion. By means of the Langevin equation it is possible to calculate such statistical properties as the autocorrelation function $C_v(t)$ of the centre of mass velocity, and the van Hove probability function [4, 5] $G_s(\mathbf{R}, t)$, which is the probability per unit volume of finding the centre of mass at $\mathbf{R}$ were it initially ($t=0$) at the origin. This function may be derived, in principle, from incoherent, inelastic neutron or light scattering, and may be computed directly with molecular dynamics algorithms [10].

Our treatment is related to that of Sears [5] who was the first to attempt a quantitative description of the model following some early remarks by Frenkel [7]. Damle *et al.* [6] later pointed out the flaws in Sears's initial equations. These are:

(*a*) Newton's third law is not accounted for correctly;
(*b*) the stochastic driving force used in the equations is assumed not to have a white spectrum while the friction terms are assumed to be time independent.

These authors then developed a version with six parameters using two initial integro-differential equations where the Langevin friction coefficients are made

time-dependent memory kernels. Here we describe a more rigorous and less parameterized treatment of the same basic idea. It is assumed that the cage of neighbours of an atom or molecule is essentially rigid and that its fluctuations in space may be represented by the translational Brownian motion of a mass m. The position of m relative to the origin at time t is denoted by a coordinate $\mathbf{r}(t)$. The vibrating atom or molecule is represented by a second particle of mass M whose position relative to the origin at time t is $\mathbf{R}(t)$. This particle is attracted towards the cage m by a restoring force proportional to the difference $[\mathbf{R}(t)-\mathbf{r}(t)]$. Finally, in order to obtain the simplest possible presentation of the theory it is assumed that the frictional force (and by inference the stochastic force) acting on M may be ignored, so that the equations of motion of the dynamical system comprising m and M are

$$m\ddot{\mathbf{r}}(t)+m\beta\dot{\mathbf{r}}(t)-M\omega_0^2[\mathbf{R}(t)-\mathbf{r}(t)]=m\dot{\mathbf{W}}(t), \tag{1}$$

$$M\ddot{\mathbf{R}}(t)+M\omega_0^2[\mathbf{R}(t)-\mathbf{r}(t)]=\mathbf{0}. \tag{2}$$

Here $m\beta\dot{\mathbf{r}}$ is the frictional force acting on m and arising from the surroundings ; $M\omega_0^2$ is the spring constant and $m\dot{\mathbf{W}}(t)$ is the force acting on m due to random collisions with its neighbours. It is assumed that $\mathbf{W}(t)$ is a Wiener process [3, 11] ; i.e.

$$\left.\begin{aligned}\langle\mathbf{W}(t)\rangle&=0,\\ \langle(\mathbf{W}(t_1)\,.\,\mathbf{e}_1)(\mathbf{W}(t_2)\,.\,\mathbf{e}_2)\rangle&=c^2\min(t_1,t_2),\end{aligned}\right\} \tag{3}$$

where $\mathbf{e}$ is a constant vector, and c a constant to be determined. Without loss of generality, one may consider, for purposes of computation, the behaviour of the ith component ($i=1, 2, 3$) of the differential equations (1) and (2) above. Thus we consider the scalar equations

$$\ddot{r}_i(t)+\beta\dot{r}_i(t)-\Omega_0^2[R_i(t)-r_i(t)]=\dot{W}_i(t), \tag{4}$$

$$\ddot{R}_i(t)+\omega_0^2[R_i(t)-r_i(t)]=0, \tag{5}$$

where

$$\Omega_0^2=\frac{M}{m}\omega_0^2. \tag{6}$$

We shall, further, write

$$W_i(t_2)-W_i(t_1)=\xi_i(t_2-t_1). \tag{7}$$

Thus if Δ denotes a time difference [3],

$$\langle\xi_i(\Delta)\rangle=0\,; \tag{8}$$

$$\langle\xi_i(\Delta)\xi_i(\Delta')\rangle=c^2|\Delta\cap\Delta'|, \tag{9}$$

where $|\ |$ denotes the length of the interval $\Delta\cap\Delta'$.

It is now convenient to write equations (4) and (5) in the matrix form

$$\dot{\boldsymbol{X}}(t)=\boldsymbol{A}\boldsymbol{X}(t)+\boldsymbol{B}\dot{\boldsymbol{W}}_i(t), \tag{10}$$

where

$$\boldsymbol{A}=\begin{bmatrix}0&0&1&0\\0&0&0&1\\-\omega_0^2&\omega_0^2&0&0\\\Omega_0^2&-\Omega_0^2&0&-\beta\end{bmatrix},\quad \boldsymbol{B}=\begin{bmatrix}0\\0\\0\\1\end{bmatrix},\quad \boldsymbol{X}=\begin{bmatrix}X_1\\X_2\\X_3\\X_4\end{bmatrix}=\begin{bmatrix}R_i\\r_i\\\dot{R}_i\\\dot{r}_i\end{bmatrix}. \tag{11}$$

2. Solution of equation (10)

The formal solution of equation (10) is :

$$\boldsymbol{X}(t)=(\exp\boldsymbol{A}t)\boldsymbol{X}_0+\int_0^t\exp[\boldsymbol{A}(t-\tau)]\boldsymbol{B}\xi(d\tau), \tag{12}$$

where $\boldsymbol{X}_0$ denotes the initial value of $\boldsymbol{X}(t)$. For our purpose it is more convenient to work with the Laplace transform $\tilde{\boldsymbol{X}}(s)$ of the solution $\boldsymbol{X}(t)$ of equation (10) rather than with $\boldsymbol{X}(t)$ directly. On writing

$$\tilde{\boldsymbol{X}}(s)=\mathscr{L}[\boldsymbol{X}(t)]=\int_0^\infty\exp(-st)\boldsymbol{X}(t)\,dt \tag{13}$$

we have

$$\mathscr{L}^{-1}\{(s\boldsymbol{I}-\boldsymbol{A})^{-1}\}=\exp\boldsymbol{A}t, \tag{14}$$

$$\mathscr{L}^{-1}\{(s\boldsymbol{I}-\boldsymbol{A})^{-1}\boldsymbol{B}\tilde{\xi}\}=\int_0^t\exp[\boldsymbol{A}(t-\tau)]\boldsymbol{B}\xi(d\tau), \tag{15}$$

where $\boldsymbol{I}$ denotes the diagonal unit matrix. From equations (8) and (9) :

$$(s\boldsymbol{I}-\boldsymbol{A})^{-1}=\frac{1}{\det(s\boldsymbol{I}-\boldsymbol{A})}\times\begin{bmatrix}s^2(s+\beta)+\Omega_0^2\,s\,;&\omega_0^2(s+\beta)\,;&s(s+\beta)+\Omega_0^2\,;&\omega_0^2\\ s\Omega_0^2\,;&s^2(s+\beta)+\omega_0^2(s+\beta)\,;&\Omega_0^2\,;&(s^2+\omega_0^2)\\ -\omega_0^2\,s(s+\beta)\,;&\omega_0^2\,s(s+\beta)\,;&s^2(s+\beta)+\Omega_0^2\,s\,;&\omega_0^2\,s\\ s^2\,\Omega_0^2\,;&-s^2\,\Omega_0^2\,;&\Omega_0^2\,s\,;&s(s^2+\omega_0^2)\end{bmatrix} \tag{16}$$

where

$$\begin{aligned}\det(s\boldsymbol{I}-\boldsymbol{A})&=s(s^3+\beta s^2+(\omega_0^2+\Omega_0^2)s+\beta\omega_0^2)\\&\equiv sF(s).\end{aligned} \tag{17}$$

Note that the matrix $\exp\boldsymbol{A}t$ is given by the inverse Laplace transform of equation (17). This matrix may be evaluated in terms of functions $g_i(t)$ ($i=1, \ldots, 4$) involving the roots of $F(s)$. Thus :

$$\exp\boldsymbol{A}t=\begin{bmatrix}g_1(t)\,;&\omega_0^2\int_0^t g_3(u)\,du\,;&\int_0^t g_1(u)\,du\,;&\omega_0^2\int_0^t g_2(u)\,du\\ \Omega_0^2\,g_2(t)\,;&\dot{g}_3(t)+\int_0^t\omega_0^2\,g_3(u)\,du\,;&\Omega_0^2\int_0^t g_2(u)\,du\,;&\int_0^t g_4(u)\,du\\ -\omega_0^2\,g_3(t)\,;&\omega_0^2\,g_3(t)\,;&g_1(t)\,;&\omega_0^2\,g_2(t)\\ \Omega_0^2\,\dot{g}_2(t)\,;&-\Omega_0^2\,\dot{g}_2(t)\,;&\Omega_0^2\,g_2(t)\,;&g_4(t)\end{bmatrix}. \tag{18}$$

These functions are tabulated below for the case where the discriminant of $F(s)$ is negative (i.e. the roots of $F(s)$ are of the form $-\sigma_1 \pm i\omega_1$; $-\sigma_2$).

Table of inverse Laplace transforms used in $\exp(\boldsymbol{A}t)$

Function	Transform represented
$g_1(t)$	$\frac{1}{1+\Gamma}\left[\left(\left(\cos\omega_1 t+\frac{(\sigma_1+\Gamma\sigma_2)}{\omega_1}\sin\omega_1 t\right)\exp(-\sigma_1 t)+\Gamma\exp(-\sigma_2 t)\right]\right.$
$g_2(t)$	$\frac{1}{[(\sigma_1-\sigma_2)^2-\omega_1^2]}\left[\left(\left(\cos\omega_1 t-\frac{(\sigma_2-\sigma_1)}{\omega_1}\sin\omega_1 t\right)\exp(-\sigma_1 t)-\exp(-\sigma_2 t)\right]\right.$
$g_3(t)$	$\frac{2\sigma_1}{[(\sigma_1-\sigma_2)^2-\omega_1^2]}\left[\left(\left(\cos\omega_1 t-\frac{(\sigma_1^2-\sigma_2^2-\omega_1^2}{2\sigma_1\omega_1}\sin\omega_1 t\right)\exp(-\sigma_1 t)-\exp(-\sigma_2 t)\right]\right.$
$g_4(t)$	$\frac{\omega_0^2-(\sigma_1^2+\omega_1^2-2\sigma_1\sigma_2)}{[(\sigma_1-\sigma_2)^2-\omega_1^2]}\left[\left(\left(\cos\omega_1 t-\frac{[(\sigma_2-\sigma_1)(\omega_0^2+\sigma_1^2)-\omega_1^2(\sigma_1+\sigma_2)]}{\omega_1[\omega_0^2-(\sigma_1^2+\omega_1^2-2\sigma_1\sigma_2)]}\right.\right.\right.$ $\left.\left.\left.\times\sin\omega_1 t\right)\exp(-\sigma_1 t)-\frac{(\sigma_2^2+\omega_0^2)\exp(-\sigma_2 t)}{\omega_0^2-(\sigma_1^2+\omega_1^2-2\sigma_1\sigma_2)}\right]\right.$
$\int_0^t g_1(u)\,du$	$\frac{1}{1+\Gamma}\left[\frac{2\sigma_1+\Gamma\sigma_2}{\sigma_1^2+\omega_1^2}\right]\left[1-\exp(-\sigma_1 t)\left(\cos\omega_1 t+\frac{(\sigma_1^2-\omega_1^2+\Gamma\sigma_1\sigma_2)}{\omega_1(2\sigma_1+\Gamma\sigma_2)}\sin\omega_1 t\right)\right.$ $\left.+\frac{\Gamma(\sigma_1^2+\omega_1^2)}{\sigma_2(2\sigma_1+\sigma_2)}[1-\exp(-\sigma_2 t)]\right]$
$\int_0^t g_2(u)\,du$	$\frac{2(2\sigma_1-\sigma_2)}{[(\sigma_1-\sigma_2)^2-\omega_1^2](\sigma_1^2+\omega_1^2)}\left[1-\exp(-\sigma_1 t)\left(\cos\omega_1 t\right.\right.$ $\left.\left.-\left[\frac{\sigma_1(\sigma_2-\sigma_1)+\omega_1^2}{\omega_1(2\sigma_1-\sigma_2)}\right]\sin\omega_1 t\right)-\frac{(\sigma_1^2+\omega_1^2)}{\sigma_2(2\sigma_1-\sigma_2)}[1-\exp(-\sigma_2 t)]\right]$
$\int_0^t g_3(u)\,du$	$\left(\frac{3\sigma_1^2-\sigma_2-\omega_1^2}{(\sigma_1^2+\omega_1^2)[(\sigma_1-\sigma_2)^2-\omega_1^2]}\right)\left[1-\exp(-\sigma_1 t)\left(\cos\omega_1 t\right.\right.$ $\left.\left.+\left[\frac{\sigma_1(\sigma_1^2-\sigma_2^2-3\omega_1^2)}{\omega_1(3\sigma_1^2-\sigma_2^2-\omega_1^2)}\right]\sin\omega_1 t\right)-\frac{2\sigma_1(\sigma_1^2+\omega_1^2)}{\sigma_2(3\sigma_1^2-\sigma_2^2-\omega_1^2)}[1-\exp(-\sigma_2 t)]\right]$
$\dot{g}_3(t)$	$\left[-\frac{[\sigma_1^2+\sigma_2^2+\omega_1^2]}{[(\sigma_1-\sigma_2)^2-\omega_1^2]}\right]\left[\exp(-\sigma_1 t)\left(\cos\omega_1 t\right.\right.$ $\left.\left.+\frac{[\sigma_1(\sigma_1^2-\sigma_2^2)+\sigma_1\omega_1^2]}{\sigma_1^2+\sigma_2^2+\omega_1^2}\sin\omega_1 t\right)+\frac{2\sigma_2\sigma_1\exp(-\sigma_2 t)}{\sigma_1^2+\sigma_2^2+\omega_1^2}\right]$
$\dot{g}_2(t)$	$\frac{-\sigma_2}{[(\sigma_1-\sigma_2)^2-\omega_1^2]}\left[\left(\cos\omega_1 t-\frac{(\sigma_1\sigma_2-\sigma_1^2-\omega_1^2)}{\omega_1\sigma_2}\sin\omega_1 t\right)\exp(-\sigma_1 t)\right.$ $\left.-\exp(-\sigma_2 t)\right]$

In the list of elements, the quantities σ_1, σ_2 and ω_1 may be related directly to ω_0^2, Ω_0^2 and β by means of Cardan's formula. The factor Γ is given by

$$\Gamma=\frac{-2\sigma_1(\sigma_1^2+\omega_1^2)}{\sigma_2(3\sigma_1^2-\sigma_2^2-\omega_1^2)}. \tag{19}$$

Having determined $\exp \boldsymbol{A}t$, the complete solution of equation (10) may be written down with the aid of equation (12), whence the averages required for the calculation of the various probability density functions may be calculated.

3. Calculation of the probability densities

We determine first the probability density function of the centre of mass velocity, $X_3(t)$. Since equation (10) is a linear differential equation, and since the random variable $W(t)$ has a gaussian probability distribution, it follows that $X_1(t)$ is a gaussian variate. Thus its p.d.f. is

$$f(X_3(t), t|X_1(0), X_2(0), X_3(0), X_4(0), 0) = \left[\frac{3}{2\pi\langle Y_3^2(t)\rangle}\right]^{3/2}\exp\left[-\frac{3\,Y_3^2(t)}{2\langle Y_3^2(t)\rangle}\right], \tag{20}$$

where for convenience we have written

$$Y_3(t)=X_3(t)-\langle X_3(t)\rangle\,; \tag{21}$$

or, in general,

$$\boldsymbol{Y}(t)=\boldsymbol{X}(t)-\langle\boldsymbol{X}(t)\rangle. \tag{22}$$

Further, by virtue of equations (8) and (12):

$$\langle\boldsymbol{X}(t)\rangle=(\exp\boldsymbol{A}t)\boldsymbol{X}_0. \tag{23}$$

Thus:

$$\boldsymbol{Y}(t)=\boldsymbol{X}(t)-(\exp\boldsymbol{A}t)\boldsymbol{X}_0 = \int_0^t \exp[\boldsymbol{A}(t-\tau)]\boldsymbol{B}\xi(d\tau). \tag{24}$$

For the problem at hand, the relevant element of $\boldsymbol{Y}(t)$ is

$$Y_3(t)=\omega_0^2\int_0^t g_2(t-\tau)\xi(d\tau) \tag{25}$$

in consequence of equations (18) and (24).

Thus by equation (9) we have

$$\langle Y_3^2(t)\rangle=\left\langle\left(\int_0^t \omega_0^2\, g_2(t-\tau)\xi(d\tau)\right)^2\right\rangle = \omega_0^4\, c^2\int_0^t g_2^2(t-\tau)\,d\tau, \tag{26}$$

where the constant c^2 is deduced from the fact that $Y_3(t)$ has the Maxwell/Boltzmann distribution in the limit of long times, i.e.

$$\lim_{t\to\infty}\langle Y_3^2(t)\rangle=\frac{3kT}{M}. \tag{27}$$

Thus it is possible, for the purposes of numerical computation, to write down the complete expression for the p.d.f. of $X_3(t)$ in terms of σ_1, σ_2 and ω_1. We do not do this explicitly here as the formulae involved are very long and cumbersome.

4. The Van Hove function $G_s(\mathbf{R}, t)$

This is the gaussian p.d.f. of $X_1(t)$, the relevant element of $\boldsymbol{Y}(t)$ being

$$Y_1(t) = \int_0^t \omega_0^2 \int_0^{t-\tau} g_2(u)\, du\, \xi(d\tau); \tag{28}$$

so that

$$\langle Y_1^2(t)\rangle = \omega_0^4 c^2 \int_0^t \left[\int_0^{t-\tau} g_2(u)\, du\right]^2 d\tau. \tag{29}$$

Thus:

$$G_s(\boldsymbol{R}_1, t) = G_s(X_1, t) = \left[\frac{3}{2\pi\langle Y_1^2(t)\rangle}\right]^{3/2} \exp\left[-\frac{3(Y_1^2(t))}{2\langle Y_1^2(t)\rangle}\right]. \tag{30}$$

5. The probability density functions in phase space

So far we have concerned ourselves with the evaluation of the p.d.f.'s of $X_1(t)$ and $X_3(t)$ only. It is also of interest to calculate the p.d.f. in phase space, i.e.

$$f(X_1(t), X_2(t), X_3(t), X_4(t), t | X_1(0), X_2(0), X_3(0), X_4(0), 0).$$

This function may be evaluated by using the following theorem about multidimensional gaussian distributions. Let $(X_1, \ldots, X_n)$ be n random variables with mean zero, then $(X_1, \ldots, X_n)$ are normally distributed in n dimensions if their p.d.f. is of the form

$$\frac{1}{(2\pi)^{n/2}(\det \boldsymbol{M})^{1/2}} \exp\left[-\tfrac{1}{2} \det(\boldsymbol{R}'\, \boldsymbol{M}^{-1}\, \boldsymbol{R})\right]; \tag{31}$$

where

$$\boldsymbol{R} = (X_1, \ldots, X_n)$$

and

$$\boldsymbol{M} = (\mu_{jk}) = (\langle x_j x_k\rangle) \tag{32}$$

is the matrix of second moments.

Since $X_1 = R_i$, $X_3 = r_i$ $(i = 1, 2, 3)$, it follows that equation (31) must be replaced by

$$\left[\frac{3}{(2\pi)^n \det \boldsymbol{M}}\right]^{3/2} \exp\left[-\tfrac{3}{2} \det(\boldsymbol{R}'\, \boldsymbol{M}^{-1}\, \boldsymbol{R})\right]. \tag{33}$$

Thus, as in the preceding cases, one may write down f from the results of the calculation of $\exp \boldsymbol{A}t$. Notice that (by analogy with the work of Chandrasekhar) equation (33) represents the so-called fundamental solution of the Fokker/Planck/Kramers equation [8, 9] for the translational itinerant oscillator.

6. The p.d.f. in configuration space

As in the two sections above, one may write down with the aid of equations (18) and (33) the p.d.f. in configuration space, viz.

$$f(X_1(t), X_3(t), t | X_1(0), X_2(0), X_3(0), X_4(0), 0) = \left[\frac{3}{4\pi^2(\langle Y_1^2\rangle\langle Y_3^2\rangle - \langle Y_1 Y_3\rangle^2)}\right]^{3/2} \times \exp\left[-\tfrac{3}{2}\left(\frac{\langle Y_3^2\rangle Y_1^2 - 2\langle Y_1 Y_3\rangle Y_1 Y_3 + \langle Y_1^2\rangle Y_3^2}{\langle Y_1^2\rangle\langle Y_3^2\rangle - \langle Y_1 Y_3\rangle^2}\right)\right]. \tag{34}$$

7. Calculation of $C_v(t)$

The autocorrelation function $C_v(t)$ of the velocity of the particle M, and its mean-square displacement, may be readily deduced from the results we have obtained for $\exp \boldsymbol{A}t$. Returning to equation (12), taking the result for its third element $X_3(t)$, multiplying this by $X_3(0)$, and averaging over all initial states of the system, we find that

$$C_v(t) = \frac{\langle \dot{R}_i(0)\dot{R}_i(t)\rangle}{\langle \dot{R}_i^2(0)\rangle} = \frac{\langle X_3(0)X_3(t)\rangle}{\langle X_3^2(0)\rangle} = g_1(t). \tag{35}$$

The mean-square displacement:

$$\langle \Delta R_i^2\rangle = \langle [R_i(t) - R_i(0)]^2\rangle \tag{36}$$

of M may be deduced from the result for $g_1(t)$, since

$$\langle \Delta R_i^2\rangle = 2\int_0^t (t-u)\langle X_3(0)X_3(u)\rangle\, du. \tag{37}$$

8. Discussion

We indicate in this section some of the experimental [1, 4] and computational [10] sources of the autocorrelation functions and probability density functions derived above and suggest ways in which the theory based on equations (1) and (2) might be improved.

A route to $C_v(t)$ is via the solution, using large digital computers, of the classical equations of motion for ensembles of about 10^2 particles [10]. Rahman [13] has carried out such a simulation of liquid argon where he derived $g_1(t)$: the mean-square displacement, and the velocity power spectrum (the Fourier transform of $g_1(t)$). The non-gaussian nature of the self van Hove function $G_s(\mathbf{R}, t)$ was discussed, and a convolution approximation put forward for calculating the distinct van Hove function [14] $G_d(\mathbf{R}, t)$ from a knowledge of $G_s(\mathbf{R}, t)$ and $g(\mathbf{R})$, the pair-distribution function (an equilibrium property measurable by X-ray diffraction [4]). The sum $G_s(\mathbf{R}, t) + G_d(\mathbf{R}, t) = G(\mathbf{R}, t)$ represents the probability of finding any particle at $\mathbf{R}$ given that there was a particle at $\mathbf{R} = 0$, at $t = 0$. The total $G(\mathbf{R}, t)$ may be equated to a macroscopic density function [4] $1/n\langle n(\mathbf{R}, t) n(\mathbf{0}, 0)\rangle$, which helps to bridge the conceptual gap between continuum and molecular dynamics in the fluid state.

Experimentally, $G_s(\mathbf{R}, t)$ may be obtained for atomic fluids by scattering thermal neutrons incoherently and inelastically, and this has been carried out for liquid argon by Dasannacharya and Rao [15]. Using, for example, the Rahman convolution, $G(\mathbf{R}, t)$ may be compared with the equivalent function obtained by polarized scattering from point scatterers of electromagnetic radiation at visible frequencies, where the normalized intensity distribution of the scattered radiation is related to $S(q, \omega)$, the double Fourier transform of $G(\mathbf{R}, t)$. (Here, q is a scalar, since the fluid is regarded as isotropic.)

The velocity p.d.f. may be obtained directly from molecular dynamics simulations [16] and any non-gaussian behaviour investigated either by the method of moments [13], or by simulating [17] a.c.f.'s of moments of the velocity, such as that of the kinetic energy, which for a gaussian velocity p.d.f. decays to a long time limit of $\frac{3}{5}$.

The problem of translation–rotation coupling in molecular fluids is of great practical interest, since nearly all the currently tractable theories of light and neutron scattering postulate in the first Born approximation a complete decoupling of these modes of motion [18, 19]. Accordingly, the neutron-scattering time-of-flight spectra, for example, are estimated in molecular fluids by factorizing the van Hove function into a product of $G(\mathbf{R}, t)$ with its orientational counterpart in the laboratory frame. It will be especially useful to produce equations (1) and (2) in a form which is both tractable analytically, and where the effect of rotation is considered on going from the internal, molecular frame to the laboratory frame within an overall structure of an itinerant oscillator model. This is a difficult problem which, when solved, could lead to more concise definitions of the overlap between hydrodynamic mode–mode coupling theories and molecular theories of ensemble fluid dynamics.

In the meantime it is relevant to point out that a form [19]

$$G(k, s) = \frac{A_0 s^2 + B_0 s + C_0}{D_0 s^3 + E_0 s^2 + F_0 s + G_0} \tag{38}$$

for the total van Hove function in (k, s) space is the basis of the Rayleigh/Brillouin structure observed in polarised light scattering. The coefficients A_0, . . ., G_0 are macroscopic (bulk and thermodynamic) quantities such as density, viscosity and specific heat. Equation (38) is precisely the form of the itinerant oscillator velocity a.c.f. in the frequency domain as derived on the basis of the classical theory of the Brownian movement.

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