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Evaluation of two-particle phase-space integrals by a reduction to three dimensions

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Abstract. Two-particle position- and momentum-dependent integrals appear in binary-collision approximations of correlation functions in the theory of fluids. We have used the Hamilton–Jacobi theory to obtain a method for reducing the dimension of such integrals from six to three for the case in which the interaction is central and continuous. The result has been used to obtain accurate evaluations of the binary collision approximations for various dynamical correlation functions. Two examples, (intermediate scattering function and longitudinal current correlation function), are presented here.

1. Introduction

A certain type of two-particle phase-space integral occurs in statistical physics [1, 2]. It appears in various correlation functions which describe the dynamics of systems of particles interacting via a central force, in particular when a binary collision expansion approximation (BCE) is used. Such six-dimensional integrals have sometimes been evaluated using Monte Carlo importance sampling, but we have found that this method cannot give the accuracy required in this kind of dynamical calculation; we use Gaussian quadrature instead. In section 2 we describe a method by which the six-dimensional phase-space integral can be reduced to a three-dimensional integral, thus allowing for improved economy and accuracy of numerical computations of these correlation functions.

This method has already been applied in calculations of the stress autocorrelation function [3], the transverse current correlation function [4] and the longitudinal current correlation function [5]. However, its derivation has not been previously presented. In this paper the method is derived and then illustrated in sections 3 and 4 by application to the density–density (intermediate scattering) function and the longitudinal current correlation function. The former contains dynamical position only, while the latter contains both position and dynamical momentum.

2. Description of method

Consider a two-particle system, each particle having mass m, with central interaction described by potential $U(r)$. The relative Lagrangian, expressed in spherical coordinates r, θ, φ is

$$L^r = m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2 \sin^2\theta\dot{\varphi}^2)/4 - U(r) \tag{1}$$

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the corresponding conjugate momenta are $p_r = m\dot{r}/2$, $p_\theta = mr^2\dot{\theta}/2$, $p_\varphi = mr^2\sin^2\theta\dot{\varphi}/2$ and the relative Hamiltonian is

$$H^r = p_r^2/m + p_\theta^2/mr^2 + p_\varphi^2/mr^2\sin^2\theta + U(r) = p^2/m + U(r). \tag{2}$$

We consider integrals of the form

$$I(t) = \int \mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}p_r\,\mathrm{d}p_\theta\,\mathrm{d}p_\varphi\,\mathrm{e}^{-p^2/m^2v_0^2}G(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}(t),\boldsymbol{p}(t)) \tag{3}$$

where $\boldsymbol{r}(t)$, $\boldsymbol{p}(t)$ are the position and momentum at time t of a particle of mass $m/2$ which has coordinates r, θ, φ, p_r, p_θ, p_φ at time $t = 0$ and then moves in the field of the central force; the temperature is mv_0^2/k_B. It is assumed that this integral is well defined for all $t \geqslant 0$; in particular, we think of G as containing a factor of $g(r)$, the pair correlation function, or its derivative $g'(r)$ corresponding to an intermolecular force model like that of Lennard-Jones.

The time dependence of the position and momentum must be calculated as accurately as possible from Newton's equation in the form

$$m\ddot{\boldsymbol{r}}(t) = 2\dot{\boldsymbol{p}}(t) = -2\nabla U(r). \tag{4}$$

Typically, a Verlet-type algorithm [6] with small time increments is used for each of the many initial states required by Gaussian quadrature to accurately evaluate the integral for the desired time range. It is, therefore, essential to express the integral in the most convenient form possible before starting the numerical computation. We present here a method by which the dimension of $I(t)$ can be reduced from six to three: this is accomplished by transforming to new coordinates to take advantage of the fact that each individual trajectory is planar. The result is a substantial gain in accuracy for computations using Gaussian quadrature methods.

Using Hamilton–Jacobi theory it is possible to find a canonical transformation from coordinates (r, θ, φ) and momenta $(p_r, p_\theta, p_\varphi)$ to new coordinates (Q_1, Q_2, Q_3) such that their conjugate momenta are the relative total energy E, angular momentum ℓ and its component ℓ_z, all of which are constants of the motion. Following standard methods [7, 8], it can be shown that Hamilton's principal function for this problem is

$$S(r,\theta,\varphi;t) = -Et + \int \mathrm{d}r\,\sqrt{m(E-U(r)) - \ell^2r^{-2}} + \int \mathrm{d}\theta\,\sqrt{\ell^2 - \ell_z^2\csc^2\theta} + \ell_z\varphi \tag{5}$$

from which the required coordinates are

$$Q_1 = \frac{\partial S}{\partial E} = -t + \int \mathrm{d}r\,\frac{m/2}{\sqrt{m(E-U(r)) - \ell^2r^{-2}}} \tag{6}$$

$$Q_2 = \frac{\partial S}{\partial \ell_z} = \varphi - \int \mathrm{d}\theta\,\frac{\ell_z\csc^2\theta}{\sqrt{\ell^2 - \ell_z^2\csc^2\theta}} \tag{7}$$

$$Q_3 = \frac{\partial S}{\partial \ell} = -\int \mathrm{d}r\,\frac{\ell r^{-2}}{\sqrt{m(E-U(r)) - \ell^2r^{-2}}} + \int \mathrm{d}\theta\,\frac{\ell}{\sqrt{\ell^2 - \ell_z^2\csc^2\theta}}. \tag{8}$$

Q_2 and $Q_3 \in [0, 2\pi)$ are the Euler angles as shown in figure 1; the third Euler angle is $\gamma \in [0, \pi]$, and $\ell_z = \ell\cos\gamma$.

Since the transformation from $r, \theta, \varphi, p_r, p_\theta, p_\varphi$ to $Q_1, Q_2, Q_3, E, \ell, \ell_z$ is canonical, its Jacobian has absolute value 1 and

$$I(t) = \int \mathrm{d}Q_1\,\mathrm{d}Q_2\,\mathrm{d}Q_3\,\mathrm{d}E\,\mathrm{d}\ell\,\mathrm{d}\ell_z\,\mathrm{e}^{-(E-U(r))/mv_0^2}\tilde{G}(Q_1, Q_2, Q_3, E, \ell, \ell_z, t) \tag{9}$$

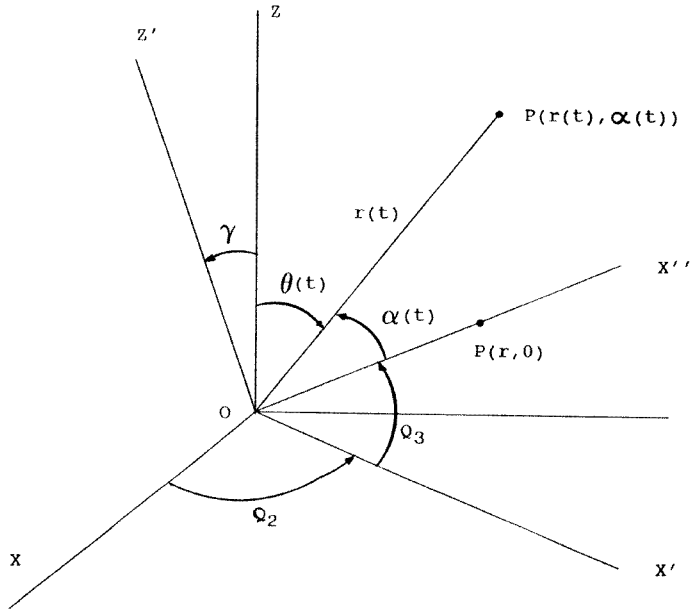

Figure 1. Q_2 is the angle between OX and the line of nodes OX′. The plane of motion of the particle P is defined by OX′ and OX″; Q_3 is the angle between OX′ and OX″. The position of the particle at time $t \geqslant 0$ is given by polar coordinates $(r(t), \alpha(t))$ measured in this plane from OX″.

where $\tilde{G}$ is G expressed in terms of the new variables. This is accomplished using the geometry of figure 1; the results for $\boldsymbol{r}(t)$, $\boldsymbol{p}(t)$ in Cartesian basis follow:

$$
\begin{aligned}
x(t) &= r(t)[\cos(Q_3+\alpha(t))\cos Q_2 - \cos\gamma\sin(Q_3+\alpha(t))\sin Q_2] \\
y(t) &= r(t)[\cos(Q_3+\alpha(t))\sin Q_2 + \cos\gamma\sin(Q_3+\alpha(t))\cos Q_2] \\
z(t) &= r(t)\sin\gamma\sin(Q_3+\alpha(t)) \\
p_x(t) &= \frac{m}{2}\dot r(t)[\cos(Q_3+\alpha(t))\cos Q_2 - \cos\gamma\sin(Q_3+\alpha(t))\sin Q_2] \\
&\quad -\frac{\ell}{r(t)}[\sin(Q_3+\alpha(t))\cos Q_2 + \cos\gamma\cos(Q_3+\alpha(t))\sin Q_2] \\
p_y(t) &= \frac{m}{2}\dot r(t)[\cos(Q_3+\alpha(t))\sin Q_2 + \cos\gamma\sin(Q_3+\alpha(t))\cos Q_2] \\
&\quad -\frac{\ell}{r(t)}[\sin(Q_3+\alpha(t))\sin Q_2 - \cos\gamma\cos(Q_3+\alpha(t))\cos Q_2] \\
p_z(t) &= \sin\gamma\left(\frac{m}{2}\dot r(t)\sin(Q_3+\alpha(t)) + \frac{\ell}{r(t)}\cos(Q_3+\alpha(t))\right).
\end{aligned}
\tag{10}
$$

In these expressions $r(t)$, $\alpha(t)$ are the polar coordinates of the particle in its plane of motion, and $\dot r(t)$ is the radial component of velocity; their initial values are $r(0) = r$, $\alpha(0) = 0$ and $\dot r(0) = \pm 2\sqrt{(E - U(r) - \ell^2/mr^2)/m}$. The subsequent values depend on r, E, ℓ, and also on the sign of $\dot r(0)$; correspondingly, the notation $r_v(t)$, $\alpha_v(t)$, $\dot r_v(t)$ is used with $v = 1$ for $\dot r(0) > 0$ and $v = -1$ for $\dot r < 0$; also, $\mathrm{d}\ell_z = -\ell\sin\gamma\,\mathrm{d}\gamma$ and $\mathrm{d}Q_1 = \frac{mr\,\mathrm{d}r}{2\sqrt{m(E-U(r))r^2-\ell^2}}$. Now (9) has the form

$$I(t) = \int \mathrm{d}r\,\mathrm{d}E\,\mathrm{d}\ell\,\frac{\mathrm{e}^{-(E-U(r))/mv_0^2} mr\ell}{2\sqrt{m(E-U(r))r^2-\ell^2}}$$

$$\times \sum_v \int_0^{2\pi} \mathrm{d}Q_2 \int_0^{2\pi} \mathrm{d}Q_3 \int_0^{\pi} \mathrm{d}\gamma\ \sin\gamma \tilde{G}_v(r, Q_2, Q_3, E, \ell, \gamma, t). \tag{11}$$

The key to the success of the method is that the time-dependent quantities in (11) depend only on r, E, ℓ and v, not on Q_2, Q_3 and γ.

It is now a technical problem to evaluate the integrals on Q_2, Q_3 and γ: the resulting integral expression will be three-dimensional and have the form

$$I(t) = \frac{m}{2} \int_0^{\infty} \mathrm{d}r\, r \int_{U(r)}^{\infty} \mathrm{d}E\, \mathrm{e}^{-(E-U(r))/mv_0^2} \int_0^{\sqrt{m(E-U(r))r}} \mathrm{d}\ell\, \frac{\ell}{\sqrt{m(E-U(r))r^2 - \ell^2}}$$
$$\times \sum_v f(r, E, \ell, r_v(t), \alpha_v(t), \dot{r}_v(t)) \tag{12}$$

where f is the value of the original G upon changing variables as described.

This method has been used to compute the BCE results for the stress autocorrelaiton function [3] and the transverse [4] and longitudinal [5] current correlation functions; however, it has not been described in detail in any of these papers. For the stress autocorrelation function the integrand of (3) is $\mathrm{e}^{-p^2/m^2v_0^2} g'(r)(z/r)F(r(t))(z(t)/r(t))$ where F is the interaction force; the calculation to reduce this integral is fairly simple because it does not involve $\boldsymbol{p}(t)$: the result is equation (44) of [3]. For the transverse current correlation function there are four terms to be reduced, all of which contain both $\boldsymbol{r}(t)$ and $\boldsymbol{p}(t)$; in particular, terms containing products like $p_x(t)p_z(t)$ appear: the result is equations (32)–(35) of [4]. The corresponding result for the longitudinal current correlation function is discussed in section 4.

3. Application to the density–density correlation function

The binary collision approximation for this correlation function was obtained by Ranganathan and Pathak [9]. In this paper we are concerned with their equations (12) and (13) which give the self and distinct two-body interaction terms. The self term is

$$F_2^{(S)}(q,t) = \frac{n\mathrm{e}^{-\frac{1}{4}q^2v_0^2t^2}}{\pi^{3/2}m^3v_0^3} \int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{p}\, g(r)\mathrm{e}^{-\frac{p^2}{m^2v_0^2}} \{\mathrm{e}^{\frac{\mathrm{i}}{2}\boldsymbol{q}\cdot[\boldsymbol{r}(t)-\boldsymbol{r}]} - \mathrm{e}^{\frac{\mathrm{i}}{2}\boldsymbol{q}\cdot[\boldsymbol{r}^0(t)-\boldsymbol{r}]}\} \tag{13}$$

where $\boldsymbol{r}(t)$ is the relative position at time t for motion in a given force field with potential $U(r)$ and $\boldsymbol{r}^0(t) = \boldsymbol{r} + 2\boldsymbol{p}t/m$ is the position of a free particle at time t; n is the density. The integral in (13) is

$$I^{(S)}(q,t) = \int \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\varphi\, \mathrm{d}p_r\, \mathrm{d}p_\theta\, \mathrm{d}p_\varphi\, g(r)\mathrm{e}^{\frac{-(H^r-U(r))}{mv_0^2}} \{\mathrm{e}^{\frac{1}{2}\mathrm{i}q[z(t)-z]} - \mathrm{e}^{\frac{1}{2}q[z^0(t)-z]}\}. \tag{14}$$

Following the procedure described in section 2, we obtain

$$I^{(S)}(q,t) = \frac{m}{2} \int_0^{\infty} \mathrm{d}r\, rg(r) \int_{U(r)}^{\infty} \mathrm{d}E\, \mathrm{e}^{-\frac{(E-U(r))}{mv_0^2}} \int_0^{\sqrt{m(E-U(r))r}} \mathrm{d}\ell\, \frac{\ell}{\sqrt{m(E-U(r))r^2 - \ell^2}}$$
$$\times \sum_v \int_0^{2\pi} \mathrm{d}Q_2 \int_0^{2\pi} \mathrm{d}Q_3 \int_0^{\pi} \mathrm{d}\gamma\ \sin\gamma \{\mathrm{e}^{\frac{1}{2}\mathrm{i}q\sin\gamma[r_v(t)\sin(Q_3+\alpha_v(t))-r\sin Q_3]}$$
$$-\mathrm{e}^{\frac{1}{2}\mathrm{i}q\sin\gamma[r_v^0(t)\sin(Q_3+\alpha_v^0(t))-r\sin Q_3]}\}. \tag{15}$$

The integral on Q_2 gives 2π and the integrals on γ and Q_3 can be evaluated by replacing the exponentials by their series representations: then each term of (15) contains the form

$$\int_0^{2\pi} \mathrm{d}Q_3 \int_0^{\pi} \mathrm{d}\gamma \sum_{j=0}^{\infty} \frac{(\mathrm{i}q)^q}{2^j\, j!} \sin^{j+1}\gamma[(r(t)\cos\alpha(t) - r)\sin Q_3 + r(t)\sin\alpha(t)\cos Q_3]^j$$

$$
\begin{aligned}
&= \sum_{j=0}^{\infty} \frac{(\mathrm{i}q)^j}{2^j\, j!} \int_0^{\pi} \mathrm{d}\gamma\ \sin^{j+1}\gamma \sum_{j'=0}^{j} \binom{j}{j'} (r(t)\cos\alpha(t) - r)^{j'} (r(t)\sin\alpha(t))^{j-j'} \\
&\quad \times \int_0^{2\pi} \mathrm{d}Q_3\ \sin^{j'} Q_3 \cos^{j-j'} Q_3 \\
&= \sum_{j=0}^{\infty} \frac{(\mathrm{i}q)^j}{2^j\, j!} \frac{\Gamma(\frac{j}{2}+1)\sqrt{\pi}}{\Gamma(\frac{j}{2}+\frac{3}{2})} \sum_{j'=0}^{j} \binom{j}{j'} (r(t)\cos\alpha(t) - r)^{j'} (r(t)\sin\alpha(t))^{j-j'} \\
&\quad \times \frac{(1+(-1)^j)(1+(-1)^{j'})}{2} \frac{\Gamma(\frac{j'+1}{2})\Gamma(\frac{j-j'+1}{2})}{\Gamma(j/2+1)} \\
&= 2\sqrt{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n q^{2n}}{2^{2n}\Gamma(n+\frac{3}{2})} \sum_{n'=0}^{n} \frac{\Gamma(n'+\frac{1}{2})\Gamma(n-n'+\frac{1}{2})}{\Gamma(2n'+1)\Gamma(2n-2n'+1)} \\
&\quad \times (r(t)\cos\alpha(t) - r)^{2n'} (r(t)\sin\alpha(t))^{2(n-n')} \\
&= 2\pi^{3/2} \sum_{n=0}^{\infty} \frac{(-1)^n q^{2n}}{2^{4n}\Gamma(n+\frac{3}{2})n!} \sum_{n'=0}^{n} \binom{n}{n'} (r(t)\cos\alpha(t) - r)^{2n'} (r(t)\sin\alpha(t))^{2(n-n')} \\
&= 2\pi^{3/2} \sum_{n=0}^{\infty} \frac{(-1)^n q^{2n}}{2^{4n}\Gamma(n+\frac{3}{2})n!} [(r(t)\cos\alpha(t) - r)^2 + (r(t)\sin\alpha(t))^2]^n \\
&= 4\pi \sum_{n=0}^{\infty} \frac{(-1)^n (q/2)^{2n}}{(2n+1)!} [r(t)^2 + r^2 - 2rr(t)\cos\alpha(t)]^n \\
&= 4\pi \frac{\sin(qD(t)/2)}{qD(t)/2} \qquad \text{where} \quad D(t)^2 = r(t)^2 + r^2 - 2rr(t)\cos\alpha(t). \qquad (16)
\end{aligned}
$$

Thus, we have obtained the three-dimensional integral expression:

$$
\begin{aligned}
I^{(S)}(q,t) &= 4\pi^2 m \int_0^{\infty} \mathrm{d}r\, r g(r) \int_{U(r)}^{\infty} \mathrm{d}E\, \mathrm{e}^{-(E-U(r))/mv_0^2} \\
&\quad \times \int_0^{\sqrt{m(E-U(r))}r} \mathrm{d}\ell\, \frac{\ell}{\sqrt{m(E-U(r))r^2 - \ell^2}} \\
&\quad \times \sum_v \left\{ \frac{\sin(qD_v(t)/2)}{qD_v(t)/2} - \frac{\sin(qD^0(t)/2)}{qD^0(t)/2} \right\}. \qquad (17)
\end{aligned}
$$

This expression contains the three distances

$$
\begin{aligned}
D_v(t) &= (r_v(t)^2 + r^2 - 2rr_v(t)\cos\alpha_v(t))^{1/2} \qquad \text{for} \quad v = \pm 1 \\
D^0(t) &= 2\sqrt{(E-U(r))/m}\, t \qquad (18)
\end{aligned}
$$

where $D_v(t)$ is the distance between a particle's initial position and its position at time t for $\dot{r} \gtrless 0$ when it moves in the given force field; $D^0(t)$ is the distance moved by a free particle during the same time interval. This is illustrated in figure 2.

The two-body term in the binary collision approximation for the distinct intermediate scattering function is

$$
F_2^{(D)}(q,t) = \frac{n\mathrm{e}^{-\frac{1}{4}q^2v_0^2t^2}}{\pi^{3/2}m^3v_0^3} \int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{p}\, g(r) \mathrm{e}^{-\frac{p^2}{m^2v_0^2}} \{\mathrm{e}^{\frac{\mathrm{i}}{2}\boldsymbol{q}\cdot[\boldsymbol{r}(t)+\boldsymbol{r}]} - \mathrm{e}^{\frac{\mathrm{i}}{2}\boldsymbol{q}\cdot[\boldsymbol{r}^0(t)+\boldsymbol{r}]}\}. \qquad (19)
$$

Using the method of this paper, the integral in (19) can be reduced to the three-dimensional expression

$$
I^{(D)}(q,t) = 4\pi^2 m \int_0^{\infty} \mathrm{d}r\, r g(r) \int_{U(r)}^{\infty} \mathrm{d}E\, \mathrm{e}^{-(E-U(r))/mv_0^2}
$$

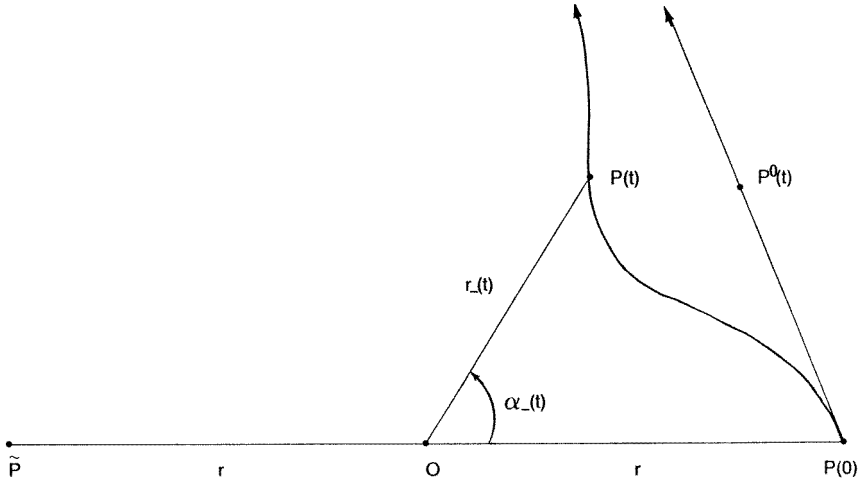

Figure 2. This figure illustrates the interpretations of the expressions (18) and (21) as distances. An actual trajectory, (which may be bound or unbound), and the corresponding free trajectory starting at $P(0) = (r, 0)$ are shown for an initial state with $\dot{r}(0) < 0$. $P(t) = (r, (t), \alpha, (t))$ is the position determined by the central force, and $P^0(t)$ is the free particle position at time $t > 0$. The distances are $D_-(t) = |P(t) - P(0)|$, $D^0(t) = |P^0(t) - P(0)|$ for the self term, and $\tilde{D}_-(t) = |P(t) - \tilde{P}|$, $\tilde{D}^0_-(t) = |P^0(t) - \tilde{P}|$ where $\tilde{P}$ is at (r, π) for the distinct term.

$$\times \int_0^{\sqrt{m(E-U(r))}r} \mathrm{d}\ell \, \frac{\ell}{\sqrt{m(E-U(r))r^2 - \ell^2}} \times \sum_v \left\{ \frac{\sin(q\tilde{D}_v(t)/2)}{q\tilde{D}_v(t)/2} - \frac{\sin(q\tilde{D}^0_v(t)/2)}{q\tilde{D}^0_v(t)/2} \right\} \tag{20}$$

where

$$\tilde{D}_v(t) = \sqrt{r_v(t)^2 + r^2 + 2r\, r_v(t)\cos\alpha_v(t)}$$

and

$$\tilde{D}^0_v(t) = \sqrt{(2r)^2 + 4m^{-1}(E - U(r))t^2 + v8rm^{-1}\sqrt{m(E-U(r))r^2 - \ell^2}}\, t. \tag{21}$$

$\tilde{D}_v(t)$ is the distance from the image point $\tilde{P}$ at (r, π) to the point $(r_v(t), \alpha_v(t))$ and $\tilde{D}^0_v(t)$ is the distance from $\tilde{P}$ to $(r^0_v(t), \alpha^0_v(t))$. This is also illustrated in figure 2.

Note that in (16) and (20) the series remaining after the reduction are expressed as elementary functions. The corresponding calculation for other correlation functions leads to convergent power series which can be evaluated numerically as required.

Numerical results for the contributions of these integrals to $F^{(S)}(q, t)$ and $F^{(D)}(q, t)$ for the Lennard-Jones potential and a chosen value of q, density and temperature are presented in section 5.

4. Longitudinal current correlation function

An expression for the BCE approximation to this function has recently been published [10]. The longitudinal viscosity requires equation (36) of that paper which gives $\phi^L(t)$ defined as

$\lim_{q\to 0}\phi^L(q,t)/q^2$: this expression can be written as

$$\begin{aligned}\phi^L(t) = 3v_0^2 &+ \frac{n}{\pi^{3/2}m^7v_0^5}\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{p}\,\mathrm{e}^{-p^2/m^2v_0^2}g(r)[2p_z^2+m^2v_0^2][p_z(t)^2-p_z^2]\\ &+\frac{n}{2\pi^{3/2}m^6v_0^5}\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{p}\,\mathrm{e}^{-p^2/m^2v_0^2}g(r)\frac{z(t)^2F(r(t))}{r(t)}[2p_z^2+m^2v_0^2]\\ &+\frac{n}{\pi^{3/2}m^5v_0^3}\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{p}\,\mathrm{e}^{-p^2/m^2v_0^2}g'(r)r^{-1}z^2[p_z(t)^2-p_z^2]\\ &+\frac{n}{2\pi^{3/2}m^4v_0^3}\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{p}\,\mathrm{e}^{-p^2/m^2v_0^2}g'(r)\frac{z^2z(t)^2F(r(t))}{rr(t)} \qquad (22)\end{aligned}$$

where F is the force. Note that two of these terms contain dynamical momentum dependence. The dimension of these integrals can be reduced to three by using the expressions in (10) and the procedure of section 2. Here the dependence on Q_2, Q_3 and γ is just the product of integer powers of sines and cosines, so the required integrals can be evaluated directly. With the substitutions $E = U(r) + mv_0^2 s$ and $\ell = mv_0 r\sqrt{s}\sin\lambda$, and the notation $\Delta U_v(t) = U(r) - U(r_v(t))$, the result is

$$\begin{aligned}\phi^L(t) = 3v_0^2 &+ \frac{4\sqrt{\pi}n}{3m}\int_0^\infty \mathrm{d}r\,r^2g(r)\int_0^\infty \mathrm{d}s\,\mathrm{e}^{-s}s^{1/2}\int_0^{\pi/2}\mathrm{d}\lambda\,\sin\lambda\sum_v \Delta U_v(t)\\ &+\frac{8\sqrt{\pi}nv_0^2}{15}\int_0^\infty \mathrm{d}r\,r^2g(r)\int_0^\infty \mathrm{d}s\,\mathrm{e}^{-s}s^{3/2}\int_0^{\pi/2}\mathrm{d}\lambda\,\sin\lambda\\ &\times\sum_v\left\{\frac{2\Delta U_v(t)}{mv_0^2}-s+\left[s\left(1-\frac{2r^2\sin^2\lambda}{r_v(t)^2}\right)+\frac{\Delta U_v(t)}{mv_0^2}\right]\cos 2(\lambda-v\alpha_v(t))\right.\\ &\left.+v\frac{\sqrt{s}\dot r_v(t)r\sin\lambda}{v_0r_v(t)}\sin 2(\lambda-v\alpha_v(t))\right\}\\ &+\frac{4\sqrt{\pi}n}{15m}\int_0^\infty \mathrm{d}r\,r^2g(r)\int_0^\infty \mathrm{d}s\,\mathrm{e}^{-s}s^{1/2}\int_0^{\pi/2}\mathrm{d}\lambda\,\sin\lambda\\ &\times\sum_v r_v(t)F(r_v(t))[5+2s(2+\cos 2(\lambda-v\alpha_v(t))]\\ &+\frac{4\sqrt{\pi}nv_0^2}{15}\int_0^\infty \mathrm{d}r\,r^3g'(r)\int_0^\infty \mathrm{d}s\,\mathrm{e}^{-s}s^{1/2}\int_0^{\pi/2}\mathrm{d}\lambda\,\sin\lambda\\ &\times\sum_v\left\{\frac{\Delta U_v(t)}{mv_0^2}(2+\cos 2\alpha_v(t))+s\left[1-\frac{2r^2\sin^2\lambda}{r_v(t)^2}\right]\cos 2\alpha_v(t)\right.\\ &\left.-s\cos 2\lambda-\frac{\sqrt{s}\dot r_v(t)r\sin\lambda}{v_0r_v(t)}\sin 2\alpha_v(t)\right\}\\ &+\frac{2\sqrt{\pi}n}{15m}\int_0^\infty \mathrm{d}r\,r^3g'(r)\int_0^\infty \mathrm{d}s\,\mathrm{e}^{-s}s^{1/2}\int_0^{\pi/2}\mathrm{d}\lambda\,\sin\lambda\\ &\times\sum_v r_v(t)F(r_v(t))[2+\cos 2\alpha_v(t)]. \qquad (23)\end{aligned}$$

Numerical evaluations of all terms of (23) have been done for various densities and temperatures using the Lennard-Jones potential and a Verlet-type algorithm to obtain the required dynamical quantities. Some of the results are given in [5].

5. Numerical results

Calculations of BCE approximations for various correlation functions have been performed using the method described in this paper. These all require knowledge of the pair correlation function $g(r)$ corresponding to the model interparticle force. Most of our calculations have used the Lennard-Jones potential with a table of $g(r)$ for each density-temperature generated from the optimized cluster theory [11]. Gaussian quadrature with many points, (Legendre for finite intervals, Laguerre for $(0, \infty)$), was used to evaluate the triple integrals, (such as (17), (20) and (23)).

An accurate dynamics calculation over the desired time range is required for each initial state (r, E, ℓ, v). We have developed an algorithm in polar coordinates which yields an approximate solution of the equations of motion

$$\ddot{r}(t) = \frac{2}{m}\left(-U'(r(t)) + \frac{2\ell^2}{mr(t)^3}\right) \qquad \dot{\alpha}(t) = \frac{2\ell}{mr(t)^2}. \tag{24}$$

The first step is chosen to be correct to fourth order in the time increment Δt, and then a Verlet-type procedure is used. For example, the second-order formulae are

$$r((j+1)\Delta t) = 2r(j\Delta t) - r((j-1)\Delta t) + \frac{2}{m}\left[\frac{2\ell^2}{mr(j\Delta t)^3} - U'(r(j\Delta t))\right]\Delta t^2$$

$$\alpha((j+1)\Delta t) = 2\alpha(j\Delta t) - \alpha((j-1)\Delta t) - \frac{4\ell\dot{r}(j\Delta t)}{mr(j\Delta t)^3}\Delta t^2$$

with

$$\dot{r}(j\Delta t) = \dot{r}((j-1)\Delta t) + \frac{2}{m}\left[\frac{2\ell}{mr(j\Delta t)^3} - U'(r(j\Delta t))\right]\Delta t \tag{25}$$

for $j \in \mathbb{N}$. A higher-order formula or smaller Δt can be used. It should be noted that such efforts to obtain high accuracy in the dynamical part of the calculation are practical only if the number of integration points is as small as possible. In fact, the main objective of this paper is to accomplish this by reducing the dimension of the integral.

The output can be tested in several ways. In particular, one-dimensional integral expressions for the first few moments were obtained, evaluated and then compared to the corresponding dynamical results for small times. Accuracy of the numerical integration was checked by considering convergence with respect to number of points. Accuracy of the dynamics was tested by convergence with respect to time increment size, by checking total energy conservation at each step and by comparison with the known result for the free-particle motion. In some cases the output can be compared to existing experimental or molecular dynamics results. Of course, to do this it is necessary to produce accurate calculations of these integrals for many states. Here we present sample results for the self and distinct parts of the intermediate scattering function using the expressions obtained in section 3.

Figure 3 shows results for the BCE approximation to the self and distinct parts of the intermediate scattering function for a selected density-temperature state and value of q. The Lennard-Jones potential with length and energy parameters σ and ε was used. Dimensionless units are $t^* = t\sqrt{48\epsilon/m\sigma^2}$, $n^* = n\sigma^3$, $T^* = v_0^{*2}/48 = mv_0^2/\varepsilon$ and $q^* = q\sigma$. In (*a*) the self free-particle term, $\mathrm{e}^{-\frac{1}{2}q^2v_0^2t^2}$, the two-particle term as computed from (13), (17) and (18) and their sums are shown. In (*b*) the distinct terms are shown: the free-particle term is $\mathrm{e}^{-\frac{1}{2}q^2v_0^2t^2} n \int \mathrm{d}\boldsymbol{r}(g(r)-1)\cos(qz)$, the two-particle term is computed from (19)–(21). These results can be used to obtain the corresponding terms of the dynamical structure factor $S(q, \omega)$.

Certain numerical results for the BCE approximation for the longitudinal current correlation function as given by (23) have been published in [5]. The total and also its

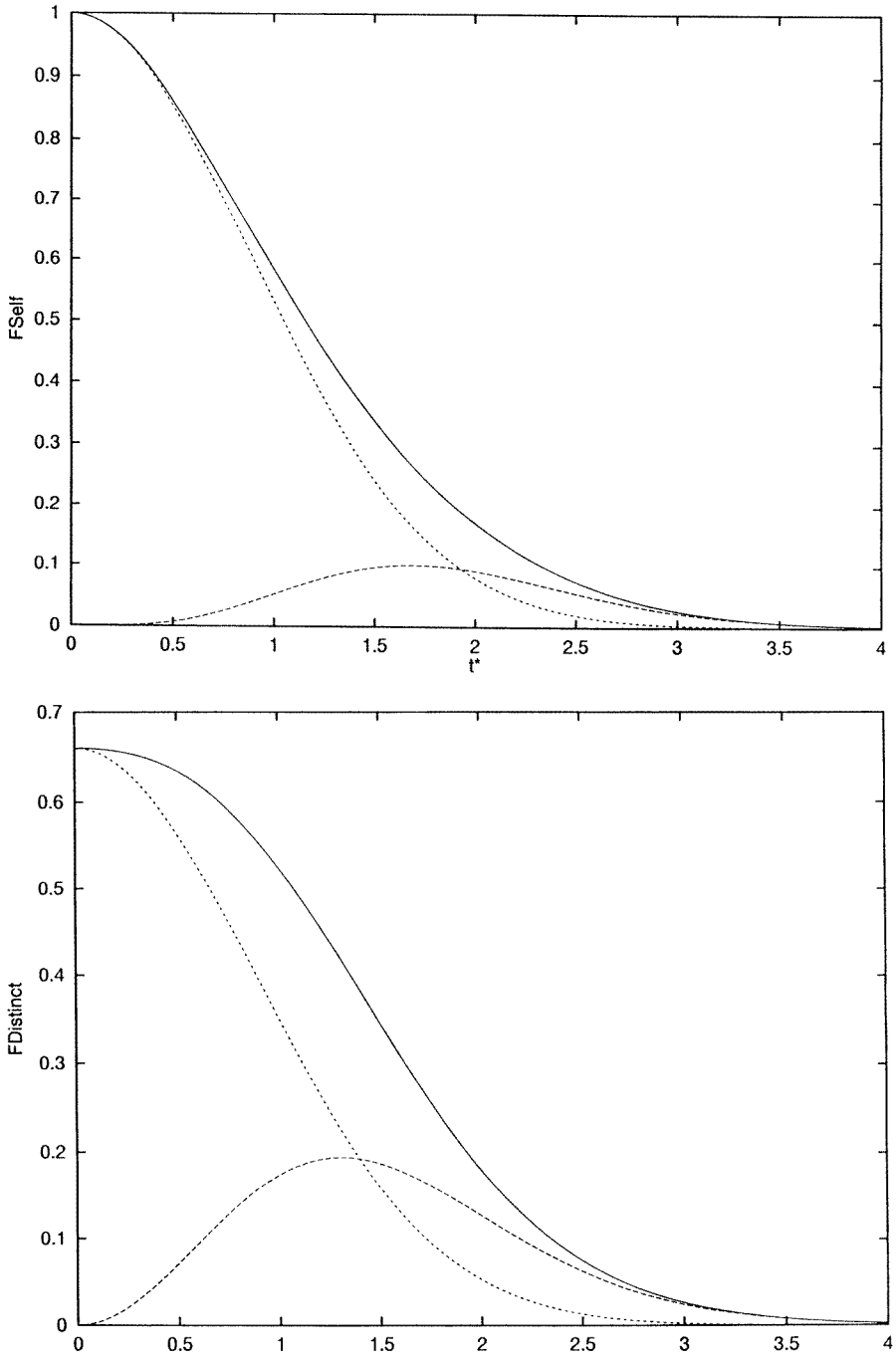

Figure 3. (*a*) BCE approximation for $F^{(S)}(q^*, t^*)$ is the solid curve. The short-dashed curve is the free-particle term and the long-dashed is the two-particle term. (*b*) The same for $F^{(D)}(q^*, t^*)$. $q^* = 6.4$, $n^* = 0.628$, $T^* = 1.47$.

components called kinetic–kinetic (sum of first three terms), kinetic–potential (fourth and fifth) and potential–potential (sixth) are displayed there. Corresponding results for the transverse current correlation function appear in [4].

These are just samples of the type of integral expressions which can be evaluated using this method. Systematic studies of BCE approximations for various correlation functions are in progress.

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