In the previous chapter, we have obtained a microscopic expression for the binary collision contribution to the memory function of the transverse current correlation function for a fluid interacting via continuous potential. It has been seen that the study is quite useful in studying the transverse viscous processes in the fluid. In the present chapter, we extend our study to obtain the binary collision contribution to the first order space-time memory function of the longitudinal current correlation function for a fluid of particles interacting through a central potential, using the cluster expansion technique. The expression obtained involves the radial distribution function and time dependence of position, momentum and acceleration of particles. We have taken the long wavelength limit of our expression which is useful in determining the time evolution of the auto-correlation of the longitudinal and bulk stresses and hence in studying the longitudinal and bulk viscosities of fluids. We have also taken the hard sphere limit of our expression for the calculation of the longitudinal and the bulk viscosity.

4.1 GENERALITIES

The longitudinal current correlation function is defined as

\[ C(q,t) = \frac{1}{N} \langle j_{xx}(q,t) j_{xx}(q,0) \rangle, \]  

where the dynamical variable \( j_{xx}(q,t) \) is given as

\[ j_{xx}(q,t) = \sum_{i=1}^{N} v_{ix}(t) e^{i q x_i(t)}, \]
with the wave vector \( \mathbf{q} \) taken along x-axis. \( v_i(t) \) and \( x_i(t) \) are the x-component of the velocity and position of the \( i \)th particle at any time \( t \). The Fourier-Laplace transform of \( C(q,t) \) is given as

\[
\tilde{C}(q,\omega) = \langle j_{xx}(q,0) | \frac{1}{\omega - \omega} | j_{xx}(q,0) \rangle.
\]

The dynamical structure factor \( S(q,\omega) \) is related to \( \tilde{C}(q,\omega) \) by the relation given as

\[
S(q,\omega) = \frac{q^2}{\omega^2} \tilde{C}(q,\omega).
\]

The time evolution of \( C(q,t) \) can be determined by using the Mori's equation of motion which in \( \omega \)-space is given as

\[
\tilde{C}(q,\omega) = - \frac{v_0^2}{\omega + \tilde{M}(q,\omega)},
\]

where \( \tilde{M}(q,\omega) \) is first-order memory function of the longitudinal current correlation function and is defined as

\[
\tilde{M}(q,\omega) = \langle Q^2 \frac{1}{\omega - \omega} | Q^2 \rangle \langle \frac{1}{\omega - \omega} | Q^2 j_{xx}(q,0) \rangle.
\]

In the above equation, \( Q = 1-P \) is the projection operator orthogonal to \( P = v_0^2 | j_{xx}(q,0) \rangle \langle j_{xx}(q,0) | \) and \( v_0^2 = k_B T/m \), is the square of the thermal speed.

The memory function \( \tilde{M}(q,\omega) \) can be expressed in terms of a conventional correlation function whose time evolution is governed by the original Liouville operator rather than the projected one \( Q^2 Q \) appearing in Eq.(4.6). By twice applying the identity

\[
\frac{\omega}{\omega - \omega} = 1 + \frac{\nu}{\nu - \omega},
\]

to Eq.(4.3) we obtain

\[
\omega^2 \tilde{C}(q,\omega) = v_0^2 \{ - \omega + \tilde{\phi}^L(q,\omega) \},
\]

where

\[
\tilde{\phi}^L(q,\omega) = \frac{1}{Nv_0^2} \langle \frac{1}{\omega - \omega} | Q^2 \rangle \langle \frac{1}{\omega - \omega} | Q^2 j_{xx}(q,0) \rangle.
\]

is the Fourier-Laplace transform of the time correlation function \( \phi^L(q,t) \). From Eqs.(4.5) and (4.8), we get
\[ \tilde{\eta}(q, \omega) = \frac{\omega \phi^L(q, \omega)}{\omega - \phi^L(q, \omega)} \quad (4.10) \]

Thus, the memory function and hence the longitudinal current correlation function can be obtained from the knowledge of the \( \phi^L(q, t) \) only. In the next section, we evaluate \( \phi^L(q, t) \) in the binary collision approximation.

4.2 EXPRESSION FOR THE BINARY COLLISION CONTRIBUTION TO THE MEMORY FUNCTION OF LONGITUDINAL CURRENT CORRELATION FUNCTION

For the dynamical variable \( j_{xx}(t) \), we have

\[ i \dot{j}_{xx} = \frac{dj_{xx}}{dt} = \sum_i \left( v_{ix} e^{i q x_i} + i q v_{ix}^2 e^{i q x_i} \right), \quad (4.11) \]

where \( v_{ix} = (-1/m) \frac{\partial U(r)}{\partial x_i} \) is the x-component of acceleration of the particle \( i \). Substituting Eq.(4.11) in Eq.(4.9), we obtain

\[ \phi^L(q, \omega) = \frac{1}{Nv_0^2} \sum_i \left\{ - \frac{1}{m} \frac{\partial U(r)}{\partial x_i} + i q v_{ix}^2 \right\} e^{i q x_i} \frac{1}{\epsilon - \omega} \]

\[ \left\{ - \frac{1}{m} \frac{\partial U(r)}{\partial x_i} + i q v_{ix}^2 \right\} e^{i q x_i} \}. \quad (4.12) \]

Eq.(4.12) can be written as sum of four terms. One is kinetic-kinetic term, two terms are kinetic-potential(cross) and the fourth term is potential-potential. We will illustrate here one of the term, i.e., potential-potential term which can be written in an alternative form as

\[ \phi^{L}_{pp}(q, \omega) = \frac{1}{m^2 v_0^2} \left\{ \frac{\partial U(r)}{\partial x_1} e^{i q x_1} \left\{ \frac{1}{\epsilon - \omega} \right\} \left[ \sum_{j \neq 1} \frac{\partial u(r_{1j})}{\partial x_1} e^{i q x_1} \right. \right. \]

\[ \left. \left. + (N-1) \sum_{j \neq 2} \frac{\partial u(r_{2j})}{\partial x_2} e^{i q x_2} \right] \right\} \quad (4.13) \]

The operator \( (\epsilon - \omega)^{-1} \) in Eq.(4.13) can be expanded by using the
binary collision expansion formula (2.68). The terms involving $(E_0 - \omega)^{-1}$ in the binary collision expansion formula are due to free particle dynamics and are evaluated as follows

$$
\phi_{pp}^L (q, \omega) = \frac{1}{m^2 v_0^2} \left\langle \frac{\partial U(r)}{\partial x_1} e^{-i \frac{r}{2}} \left\{ \frac{1}{E_0 - \omega} \right\} \sum_{j \neq 1} \frac{\partial u(r_j)}{\partial x_1} e^{i q x_1} \right\rangle + (N-1) \sum_{j \neq 2} \frac{\partial u(r_j)}{\partial x_2} e^{i q x_2}.
$$

(4.14)

The sum over $j$ in the last term of Eq.(4.14) can be simplified by noting that all terms except for $j=1$ are equivalent. Thus

$$
\sum_{j \neq 2} \frac{\partial u(r_j)}{\partial x_2} e^{i q x_2} = \frac{\partial u(r_2)}{\partial x_2} e^{i q x_2} + (N-2) \frac{\partial u(r_3)}{\partial x_2} e^{i q x_2}.
$$

(4.15)

By using Eq.(4.15) we can write Eq.(4.14) in time domain as

$$
\phi_{pp}^L (q, t) = \frac{1}{p_0^2} \left\langle e^{-i \frac{r}{2}} \left\{ (N-1) \frac{\partial u(r_2)}{\partial x_1} e^{-i q x_1} - (N-1) \frac{\partial u(r_2)}{\partial x_1} e^{-i q x_2} \right\} + \frac{\partial u(r_3)}{\partial x_2} e^{-i q x_2} \right\rangle.
$$

(4.16)

The first two terms in the above equation contain dynamics of two particles while the last term contains interaction of three particles. By following the procedure of averaging, as given in chapter-3, the final expression for $\phi_{pp}^L (q, t)$ is written as

$$
\phi_{pp}^L (q, t) = \frac{n I_0}{\beta p_0} \int \frac{d \mathbf{r} d \mathbf{p}}{v_2} \frac{\partial g(r)}{\partial x} g\left\{ \frac{p}{v_2} \right\} e^{i q x/2}
$$
Writing the total potential as a sum of pair potential, the contribution due to second term of BCE formula in Eq.(4.13) can be written as

\[ \phi^{\perp}_{pp_1}(q,\omega) = \frac{1}{m v_0^2} \frac{\partial \Phi}{\partial x_1} e^{iq x_1} \left\{ \sum_{l \neq k} \left( \frac{1}{\xi_0} - \frac{1}{\xi_1(1,k)} - \frac{1}{\xi_0 - \omega} \right) \right\} + (N-1) \sum_{j \neq 2} \frac{\partial u(r_{1j})}{\partial x_1} e^{iq x_1} \left\{ e^{i \xi_{12} t} - e^{-i \xi_{12}(0) t} \right\} \]

By using Eq.(4.15), the above equation in time domain is written as

\[ \phi^{\perp}_{pp_1}(q,t) = \frac{1}{p_0^2} \frac{\partial \Phi}{\partial x_1} \left\{ e^{iq x_1} \left\{ e^{i \xi_{12} t} - e^{-i \xi_{12}(12) t} \right\} \right\} + (N-1) \frac{\partial u(r_{12})}{\partial x_1} e^{-iq x_1} \left\{ e^{i \xi_{12} t} - e^{-i \xi_{12}(12) t} \right\} \]

where

\[ \xi_{12} = \xi_0(1) + \xi_0(2) + \xi_1(12) = \xi_0(12) + \xi_1(12). \]

In the first two terms of Eq.(4.19), dynamics of only two particles appear whereas the last term involves interaction of three particles and is proportional to square of the density. It is shown in Appendix D that for the hard sphere fluid for recollision process the three particle terms contribute to the binary collision dynamics. The dynamics of two particles that appears in the first two terms of Eq.(4.19) has to be averaged over the initial equilibrium configuration of the system. After performing this average, the result can be written as
where $g(r)$ and $G(P)$ defined in chapter-3, are the static pair correlation function and Maxwellian momentum distribution, respectively. Following the procedure as described in chapter-3, Eq.(4.20) simplifies to an expression given as

$$
\phi_{PP_1}^L (q,t) = \frac{n_I^2}{\beta P_0^2} \int \mathcal{d}r \mathcal{d}r_1 \mathcal{d}p \mathcal{d}p_1 \mathcal{d}p_2 \frac{\partial g(r_{12})}{\partial x_1} \left[ G(P_1) \left[ e^{i q x_1} \left\{ e^{-i q x_1} \frac{\partial u(r_{12})}{\partial x_1} - e^{-i q x_2} \frac{\partial u(r_{12})}{\partial x_1} \right\} \right] \right],
$$

(4.20)

Using the procedure outlined above we can evaluate all the terms in Eq.(4.12) in the binary collision approximation. Writing

$$
\phi^L (q,t) = \phi_0^L (q,t) + \phi_1^L (q,t),
$$

where $\phi_0^L (q,t)$ and $\phi_1^L (q,t)$ represent respectively in time domain the contributions corresponding to the first and second term of binary collision expansion formula. These are obtained to be as given below

$$
\phi_0^L (q,t) = N_0^2 \left[ 3 - 6a^2 + a^4 \right] e^{-a^2/2} + \frac{i n_o N}{P_0^3} \int \mathcal{d}r \mathcal{d}p \left[ G \left( \frac{P}{\sqrt{2}} \right) \left\{ \exp \left[ i q x \left( \frac{P}{m} \right) \right] \right\} \right],
$$

(4.21)
\[ \phi_i(q,t) = \frac{n\Omega_0^2}{P_0^4} \int drdp \ G \left( \frac{p}{\sqrt{2}} \right) \ g(r) \ e^{-iqx/2} \left[ A_0 [p_x(t)] e^{-iqx(t)/2} - e^{iqx(t)/2} \right] F_x \left\{ |r + \frac{pt}{m}| \right\} \] (4.22)
Eqs. (4.22) and (4.23) contain only the two particle collisions. The second and third terms containing force of the form $F(r + \frac{p t}{m})$ in Eq. (4.22) are divergent due to the appearance of free particle dynamics in the argument of force. These terms cancel exactly with the same divergent terms appearing in Eq. (4.23). However, the final result for $\phi^{i}(q,t)$ does not diverge and gives an exact low density result given as

$$\phi^{i}(q,t) = \Omega_{0}^{2} \left[ 3 - 6a^{2} + a^{4} \right] e^{-a^{2}/2}$$

$$+ \frac{n_{0}^{2}}{\beta p_{0}^{3}} \int dr dp \left\{ \frac{p}{\sqrt{2}} \right\} g(r) \left[ e^{(iq/2)[x-x(t)]} B[p_{x}(t)]
+ e^{(iq/2)[x + x(t)]} B[-p_{x}(t)]
- e^{-iq[x + (p_{x}t / 2m)]} B_{0}[-p_{x}] \right\}$$

$$+ \frac{n_{0}^{2}}{\beta p_{0}^{3}} \left[ \int dr dp \left\{ \frac{p}{\sqrt{2}} \right\} g(r) e^{iqx/2} A_{0}[p_{x}] \left[ \left\{ e^{-iq(t)/2}
- e^{iq(t)/2} \right\} F_{x}(r(t)) \right] \right]$$

$$- \frac{n_{0}^{2}}{\beta p_{0}^{3}} \left[ \int dr dp \left\{ \frac{p}{\sqrt{2}} \right\} \frac{\partial g(r)}{\partial x} e^{iqx/2} \left[ A[p_{x}(t)] e^{-iq(t)/2} \right] \right]$$
+A[-p_x(t)]e^{iqx(t)/2 - A_0[p_x] e^{(-iq/2)[x + (p_x t/m)]}}

-A_0[-p_x] e^{(iq/2)[x + (p_x t/m)]}

\[ + \frac{n I_0}{\beta p_0^2} \int dr dp \left( \frac{p^2}{\sqrt{2}} \right) \frac{\partial g(r)}{\partial x} e^{iqx/2} \]
\[
\left[ \left( e^{-iqx(t)/2} - e^{iqx(t)/2} \right) \right] F_X(r(t)). \quad (4.24)
\]

In these equations, we have introduced the following notations:

\( I_0 = q v_0 \); \quad \alpha = \Omega_0 t, \quad (4.25)

\( I_n \equiv I_n(q,t) = \int dp G(\sqrt{2}p) p^n e^{-(iqp_x/m)t}. \quad (4.26) \)

\[ A[p_x(t)] = (1/4) p_x^2(t) I_0 + p_x(t) I_1 + I_2. \quad (4.27) \]

and

\[ B[p_x(t)] = (1/16) p_x^2 p_x^2(t) I_0 + (1/4) (p_x p_x^2(t) + p_x^2 p_x(t)) I_0 + I_1 + (1/4) [p_x^2 + p_x^2(t) + 4 p_x p_x(t)] I_2 + [p_x + p_x(t)] I_3 + I_4. \quad (4.28) \]

\( A_0 \) and \( B_0 \) are the values of \( A \) and \( B \) with \( p_x(t) = p_x(0) = p_x \).

In Eq.(4.24), the position and momentum vectors \( r(t) \) and \( p(t) \) of the particle moving in a central potential may be determined from the equation of motion given by Eq.(3.34). In the next section, we obtain an expression for the longitudinal and bulk viscosities from the long wavelength limit of Eq.(4.24).

### 4.3 LONGITUDINAL AND BULK VISCOSITIES

The expression for the longitudinal viscosity as given in chapter-2 is

\[
\eta' = \beta n m^2 \int_0^\infty \left[ \frac{q^2}{q} \frac{\phi^l(q,t)}{q} \right. + \left. \langle J_{xx} \rangle \langle J_{xx}(t) \rangle - \langle J_{xx}(t) \rangle \langle J_{xx} \rangle \right] dt,
\]

\[
- \langle J_{xx} \rangle \langle J_{xx}(t) \rangle \right] dt, \quad (4.29)
\]
where \( \langle J_{\alpha\beta} \rangle \) is given by Eq. (2.33). In Eq. (4.30), \( S^1(t) \) is \( m^2 \) times the integrand of Eq. (4.29). The expressions for the bulk and the shear viscosities are similar to Eq. (4.30) and are given respectively, as

\[
\eta^\alpha = \beta n \int_0^\infty S^\alpha(t) \, dt; \quad S^\alpha(t) = \sum_{\alpha, \beta} \langle J_{\alpha\alpha} - J_{\alpha\beta} \rangle \langle J_{\beta\beta} \rangle. \tag{4.31}
\]

and

\[
\eta^S = \beta n \int_0^\infty S^S(t) \, dt; \quad S^S(t) = \langle J_{xy}(t) J_{xy}(0) \rangle. \tag{4.32}
\]

The longitudinal, shear and bulk viscosities are related to each other by the relation

\[
\eta^l = \frac{4}{3} \eta^S + \eta^B. \tag{4.33}
\]

This implies that

\[
S^1(t) = \frac{4}{3} S^S(t) + S^B(t). \tag{4.34}
\]

Using the above relation, we note that

\[
\langle J_{xx}(t) J_{yy}(0) \rangle = \langle J_{xx}(t) J_{xx}(0) \rangle - 2 \langle J_{xy}(t) J_{xy}(0) \rangle. \tag{4.35}
\]

The expression for \( Lt \to \phi^L(q, t) \) appearing in Eq. (4.29) can be obtained from Eq. (4.24) and is given as

\[
\phi^L(t) = \int_{q \to 0} \frac{\phi^L(q, t)}{q^2} = \frac{3k_B T}{m} + \frac{n}{m^2 p_0^2} \left\{ \int dr dp \frac{p^2}{v^2} \right\} g(r) \\
+ \frac{n}{m p_0^2} \left\{ \int dr dp \frac{p^2}{v^2} \right\} g(r) \left[ \frac{p_x^2 I_0(q) + I_2}{2} \right] x(t) F_X(r(t))
\]
The above expression contains effects of all uncorrelated binary collisions. The derivative of $g(r)$ appears in some terms of above equation so the density dependence is more complicated than the explicit linear dependence. In Eq. (4.36), the first two terms represent the purely kinetic-kinetic terms corresponding to the transport of momentum via the displacement of particles, the third and fourth terms are the kinetic-potential(cross) terms, whereas the last term is due to the potential-potential term arising from the action of interparticle forces. Eq. (4.36) at $t = 0$ reduces to

$$
\phi^l(0) = \frac{3kT}{m} + \frac{n}{m} \int dr g(r) x x(t) F_x(r(t)) + \frac{n}{2m} \int dr \frac{\partial g(r)}{\partial x} x^2 F_x(r).
$$

(4.37)

This is an exact expression for the second sum rule of the longitudinal current correlation function in the long wavelength limit.

The kinetic contribution to $<J_{xx}(t)>$ is given by

$$
<J_{xx}(t)> = \sum_i \frac{p_{ix}^2(t)}{3m}.
$$

(4.38)

Using this equation, we write the second term of Eq.(4.29) as

$$
<J_{xx}(t)><J_{xx}(0)> = \frac{1}{9m^2} \sum_{i,j} <p_{ix}^2(t) p_{jx}^2(0)>.
$$

(4.39)

The ensemble average in the above equation involves terms like $<p_{ix}^2(t) p_{jx}^2>$ and $<p_{ix}^2(t) p_{jy}^2>$. The former term can be related to the kinetic part of $\phi^l(t)$ whereas, the later can be related to kinetic part of $\phi^t(t)$ and $\phi^l(t)$ (i.e., transverse stress correlation function). Using Eq.(4.35) in Eq.(4.39), we finally
obtain
\[
\langle \langle J_{xx}(t) \rangle \rangle = \left\langle \left\langle \frac{1}{3} \phi_{kk}^T(t) - \frac{4}{3} \phi_{kk}(t) \right\rangle \right\rangle.
\] (4.40)

Similarly, the other two terms in Eq.(4.29) for the non-interacting part are
\[
\langle J_{xx}(0) \rangle = \left\langle \left\langle \frac{1}{3} \phi_{kk}^T(t) - \frac{4}{3} \phi_{kk}(t) \right\rangle \right\rangle.
\] (4.41)

In the above equation, the subscript kk represents the kinetic-kinetic part of the correlation functions. Using Eqs.(4.40) and (4.41) in Eq.(4.29) and taking into account for only kinetic-kinetic contribution, we obtain
\[
S_{kk}^T(t) = \phi_{kk}^T(t) + \left\langle \left\langle \frac{1}{3} \phi_{kk}(t) - \frac{4}{3} \phi_{kk}(t) \right\rangle \right\rangle - 2 \left\langle \left\langle \frac{1}{3} \phi_{kk}(t) - \frac{4}{3} \phi_{kk}(t) \right\rangle \right\rangle - \frac{4}{3} \phi_{kk}(t).
\] (4.42)

This implies that the kinetic part of the longitudinal stress correlation function is \( \frac{4}{3} \) times the kinetic part of the transverse stress correlation function. In terms of viscosities, we obtain
\[
\eta_{kk}^T = \frac{4}{3} \eta_{kk}^S.
\] (4.43)

and the relation (4.33) provides that the kinetic contribution to the bulk viscosity, \( \eta^b \), is always zero.

In the next section, we evaluate the longitudinal and the bulk viscosities for a system interacting via hard sphere potential within the binary collision approximation.

4.3.1 HARD SPHERE LIMIT

In order to calculate the longitudinal viscosity \( \eta^l \), we have to calculate the various terms in Eq.(4.29). An expression for the first term given by Eq.(4.29) can be evaluated by using the well known hard sphere dynamics whereas, the last three terms can be simplified for the hard sphere potential in a manner given below.
We write Eq.(2.33) given in chapter-2 as

\[ <J_{xx}> = PV + V \left\{ \frac{\partial P}{\partial T} \right\} \left\{ \frac{\partial E}{\partial T} \right\}^{-1} \left\{ E - \bar{E} \right\}. \] (4.44)

From the equation of state[9] for the hard sphere, we have

\[ \frac{PV}{k_B T} = 1 + \nu. \] (4.45a)

\[ E = \frac{3}{2} k_B T. \] (4.45b)

\[ \frac{\partial E}{\partial T} = C_v = \frac{3}{2} k_B. \] (4.45c)

\[ \frac{\nu P}{\partial T} = k_B (1 + \nu). \] (4.45d)

where \( \nu = \frac{2}{3} \pi n \sigma^3 g(\sigma) \). Using the above equations in Eq.(4.44), obtain

\[ <J_{xx}(t)> = \sum_i \frac{P_i^2(t)}{3m} \left[ 1 + \nu \right]. \] (4.46)

Now considering the second term of Eq.(4.29), i.e., \( <<J_{xx}>J_{xx}(t)>> \) we write it by using Eq.(4.46) as

\[ <<J_{xx}>J_{xx}(t)>> = p_1^2(t) p_1^2(0) \frac{1}{9m^2} \left[ 1 + \nu \right]^2. \] (4.47)

Using Eq.(4.35), we express Eq.(4.47) as

\[ <<J_{xx}(t)> J_{xx}(0)>> = (1 + \nu)^2 \left[ \phi_{kk}^l - \frac{4}{3} \phi_{kk}^T \right]. \] (4.48)

Similarly, other two terms of Eq.(4.29) can be written as

\[ <J_{xx}(t) J_{xx}> = \left[ 1 + \nu \right]^2 \left[ \{ \phi_{kp}^l - \frac{4}{6} \phi_{kp}^T \} + \{ \phi_{kk}^l - \frac{4}{3} \phi_{kk}^T \} \right]. \] (4.49)

and

\[ <J_{xx} J_{xx}(t)> = \left[ 1 + \nu \right]^2 \left[ \{ \phi_{kp}^2 - \frac{4}{6} \phi_{kp}^T (t) \} + \{ \phi_{kk}^2 - \frac{4}{3} \phi_{kk}^T \} \right]. \] (4.50)

where \( \phi_{kp}^l \) and \( \phi_{kp}^2 \) are the terms corresponding to two cross terms.

Now collecting the terms which are independent of density, we obtain relation (4.42). Using the result for the shear viscosity for a hard sphere, obtained in chapter-3, we obtain

65
\[ \eta_{kk}^i = \frac{4}{3} \left[ \frac{5(k_B T_m)^{1/2}}{16 \sqrt{\pi} \ g(\sigma) \ \sigma^2} \right]. \quad (4.51) \]

Now, we collect the terms proportional to density appearing in Eqs. (4.48)-(4.50) corresponding to cross terms in Eq. (4.29) we obtain
\[ S_{kp}^i(t) = \phi_{kp}^L(t) + \frac{4n\sigma^3}{3} g(\sigma) \left( \phi_{kk}^L(t) - \frac{4}{3} \phi_{kk}^T(t) \right) \]
\[ - \frac{4n\sigma^3}{3} g(\sigma) \left( \phi_{kk}^L(t) - \frac{4}{3} \phi_{kk}^T(t) \right) \]
\[ - \left( \phi_{kp}^L(t) - \frac{4}{3} \phi_{kp}^T(t) \right). \]
\[ = \frac{4}{3} \phi_{kp}^T(t). \quad (4.52) \]

which in turn implies that \( \eta_{kp}^i = \frac{4}{3} \eta_{kp}^s \). Using our earlier result, obtained in chapter-3, for \( \eta_{kp}^s \) within the binary collision approximation we obtain
\[ \eta_{kp}^i = \frac{4}{3} \left[ \frac{5(k_B T_m)^{1/2}}{16 \sqrt{\pi} \ \sigma^2} \right] \frac{0.8 \nu}{g(\sigma)} = \eta_0 \frac{16 \nu}{15 \ g(\sigma)}. \quad (4.53) \]

Similarly, we collect the terms corresponding to potential contribution to viscosity, i.e., terms proportional to square of density, we obtain
\[ S_{pp}^i(t) = \phi_{pp}^L(t) + \nu^2 \left[ \phi_{kk}^L(t) - \frac{4}{3} \phi_{kk}^T(t) \right] \]
\[ - \nu \left[ \phi_{kp}^L(t) + \phi_{kp}^T(t) - \frac{4}{3} \phi_{kp}^T(t) \right]. \quad (4.54) \]

This expression does not express potential-potential contribution to longitudinal viscosity in terms of the contribution to shear viscosity alone as is done in Eqs. (4.42) and (4.52). This is due to the fact that the contribution to the bulk viscosity is mainly due to the potential-potential part of the stress. In order to determine the potential-potential contribution to the longitudinal viscosity, we need to evaluate various contributions due to \( \phi_{kk}^T \).
\( \phi_{kk} \) and \( \phi_{kk}^{L} \) for the hard sphere interaction.

Considering the kinetic-kinetic part of Eq.(4.36) which is given as

\[
\phi_{kk}^{L}(t) = \frac{3k_B T}{m} + \frac{n}{m^2 p_0^2} \int \int d\mathbf{r} d\mathbf{p} \ g\left(\frac{\mathbf{p}}{\sqrt{2} \mathbf{v}}\right) g(r) \chi \left[ \frac{I_0}{8} \left( p_x^2 p_x(t) - p_x^4 \right) + \frac{I_2}{2} \left( p_x^2(t) - p_x^2 \right) \right].
\] (4.55)

The time dependence of above equation is determined by taking its derivative w.r.t. time which is given as

\[
\frac{d\phi_{kk}^{L}(t)}{dt} = \frac{n}{m^2 p_0^2} \int \int d\mathbf{r} d\mathbf{p} \ g\left(\frac{\mathbf{p}}{\sqrt{2} \mathbf{v}}\right) g(r) \left[ p_x^2 p_x(t) \dot{p}_x(t) \frac{I_0}{4} + I_2 p_x(t) \dot{p}_x(t) \right].
\] (4.56)

First term in this equation is solved in Appendix C at t=0. The result obtained there is given as

\[
\frac{d\phi_{kk}^{L}(t)}{dt} \bigg|_{t=0} = - \frac{48}{5} n g(\sigma) \sigma^2 v_0^3 v n.
\] (4.57)

Writing

\[
\phi_{kk}(t) = \phi_{kk}^{L}(t=0) + \frac{d\phi_{kk}^{L}(t)}{dt} \bigg|_{t=0} t + \ldots.
\] (4.58)

The next and higher order terms in the above expansion involve the correlated binary collisions. Ignoring all these terms, we approximate \( \phi_{kk}(t) \) to decays as

\[
\phi_{kk}(t) = \phi_{kk}(0) \exp\left(-t/\tau_{R}^{-1}\right) ; \tau_{R}^{-1} = \frac{d\phi_{kk}(t)}{dt} \bigg|_{t=0} / \phi_{kk}(0).
\] (4.59)

The contribution to the longitudinal viscosity corresponding to first term in Eq.(4.56) in the binary collision approximation for kinetic-kinetic part is obtained to be
\[ \eta_{kk}^{l} = - \frac{\text{nm} \, \phi_{kk}^2(0)}{\left[ \frac{d\phi_{kk}(t)}{dt} \right]_{t=0}} \]

\[ = \frac{15(k_B T_m)^{1/2}}{16 \sqrt{\pi} \, g(\sigma) \, \sigma^2}. \]  

By adopting the similar procedure as is used to solve the first term in Eq.(4.56) the contribution from the second term is given as

\[ \frac{d\phi_{kk}^{l2}(t)}{dt} \bigg|_{t=0} = - \frac{8}{3} \, n g(\sigma) \, \sigma^2 v_0^2 \sqrt{\pi} \]  

whose contribution to the longitudinal viscosity is given by

\[ \eta_{kk}^{l2} = \frac{3(k_B T_m)^{1/2}}{8\sqrt{\pi} \, g(\sigma) \, \sigma^2}. \]  

The total kinetic contribution arising due to \( \phi^{l}(t) \) in Eq.(4.36) is then given by

\[ \eta_{kk}^{l} = \eta_{kk}^{l1} + \eta_{kk}^{l2} = \frac{21(k_B T_m)^{1/2}}{16\sqrt{\pi} \, g(\sigma) \, \sigma^2}. \]  

Here, it may be noted that \( \eta^{l1} \) is the contribution to the longitudinal viscosity \( \eta^{l} \) due to \( \phi^{l}(t) \) alone. Now, we take the kinetic-potential(cross) contribution to \( \phi^{l}(q,t) \). The binary collision expression for \( \phi_{kp}^{l1}(t) \) is given by the third term of Eq.(4.36) given below

\[ \phi_{kp}^{l1}(t) = \frac{n}{m \pi^2} \int \int dr dp G \left\{ \frac{p}{\sqrt{2}} \right\} g(r) \left[ (p_x^2 I_0/4) + I_2 \right] x(t) F_x(x(t)). \]  

The two terms in this equation can be solved in a similar manner as we have solved the kinetic-kinetic term in Appendix C. Thus

\[ \phi_{kp}^{l1}(t) \bigg|_{t=0} = \left[ \frac{22}{15} + \frac{2}{3} \right] g(\sigma) \, \sigma^3 v_0^2 \, n \, \pi. \]

\[ = \frac{16}{5} \, v_0^2. \]
The time dependent part of second cross term appearing in Eq.(4.36) is simplified to
\[ \phi_{kp}^{L}(t) \bigg|_{t=0} = 5 \nu_0^2. \] (4.66)

Total cross contribution arising due to \( \phi_{kp}^{L} (t) \) is then given by
\[ \phi_{kp}^{L} (t) \bigg|_{t=0} = \frac{21}{5} \nu_0^2. \] (4.67)

The corresponding contribution to the viscosity due to both the cross terms is obtained to be
\[ \eta_{kp}^{L} = \phi_{kp}^{L} (t) \bigg|_{t=0} \tau_{R} = \frac{5}{16 \sigma^2 \sqrt{n} g(\sigma) \nu_0}. \] (4.68)

where \( \eta_0 = \frac{5 (k_B T_m)^{1/2}}{16 \sigma^2 \sqrt{n}} \).

The potential-potential term of Eq.(4.36) is written as
\[ \phi_{pp}^{L1}(t) = \frac{n I_0}{2 \beta^2_0} \int_{-1}^{0} dp G \left( \frac{p}{\sqrt{2}} \right) \frac{d g(r)}{d r} \frac{x(t)}{r} \times x(t) F_y(r(t)). \] (4.69)

Writing \( g(r) = - y(r) \exp(-\beta u(r)), \) where \( y(r) \) is continuous function even when both \( g(r) \) and \( u(r) \) have discontinuities, we obtain
\[ g'(r) = y'(r) \exp(-\beta u(r)) + g(r) \delta(r - \sigma^+). \] (4.70)

The first term in Eq.(4.70) is non zero only when \( r > \sigma \). So, we neglect the first term and the \( \delta \)-function in the second term yields \( \tau = 0 \) and hence \( x(t) = x(0) \). So, Eq.(4.69) reduces to
\[ \phi_{pp}^{L1} (t) = \frac{n I_0}{\beta^2_0} \int_{-1}^{0} dp G \left( \frac{p}{\sqrt{2}} \right) g(r) \delta(r-\sigma) \frac{x(t)}{r^2} \theta(\sigma^2 - b^2) \theta(-\mu) \delta(t). \]
\[ = \frac{n I_0}{\beta^2_0} \sigma^4 4\pi \int_{0}^{2\pi} d\phi \int_{0}^{1} d\mu \mu \theta(-\mu). \] (4.71)

The \( \delta \)-function restricts the range of \( \mu \) integration from -1 to 0.
and we get
\[ \phi_{pp}^L (t) = \frac{4}{5} \nu \pi n \sigma^4 v_0 g(\sigma) \delta(t). \]  
(4.72)

By using the definition of the longitudinal viscosity, we have for the potential-potential contribution, due to \( \phi^L(t) \), to the longitudinal viscosity
\[ \eta_{pp}^L (t) = \frac{4}{5} \nu \pi n \sigma^4 v_0 g(\sigma)(k_B T m)^{1/2}. \]  
(4.73)

The last term in Eq.(4.19) which appears as proportional to \( n^2 \) can contribute to the longitudinal viscosity in the binary collision approximation if the collisions, which are uncorrelated, are separated out. However, this term can not be reduced to order \( n \) for the binary collision contribution for a continuous potential. It is noted that the last term of Eq.(4.19) is the only such term which provides a contribution to the longitudinal viscosity of order \( n^2 \). The evaluation of this term is given in the Appendix D. The result obtained there is given as
\[ \phi_{pp}^{L2} (t) = -\frac{n}{5} \sigma^4 \nu \pi g(\sigma) v_0 \delta(t), \]  
(4.74)

whose contribution to the longitudinal viscosity is then given by
\[ \eta_{pp}^{L2} = \frac{1}{5} \sigma^4 n^2 \nu \pi g(\sigma) (k_B T m)^{1/2}. \]  
(4.75)

The total contribution of potential-potential term to the longitudinal viscosity is then given by the sum of Eqs.(4.73) and (4.75) which is given as
\[ \eta_{pp}^L = \frac{36}{5n} \eta_0 v^2 g(\sigma). \]  
(4.76)

Using the Green-Kubo relation for Eq.(4.54) and substituting the various contributions from Eqs.(4.63),(4.68) and (4.76) we obtain an expression for the potential-potential contribution to the longitudinal viscosity given as
\[ \eta_{pp}^1 = \frac{36 \nu^2}{5 \nu \pi \, g(\sigma)} \eta_0 - \frac{4 \nu^2}{15 \nu \pi \, g(\sigma)} \eta_0. \]  
(4.77)

The last term in the above equation appears due to the subtraction of invariant term from \( J_{xx}(t) \).

The complete expression for the longitudinal viscosity is sum of Eqs. (4.51), (4.53) and (4.77) and is given as

\[ \eta^l = \frac{\eta_0}{g(\sigma)} \left[ \frac{4}{3} + \frac{16}{15} \nu + \frac{36}{5 \pi} \nu^2 - \frac{4}{15} \nu^2 \right]. \]  
(4.78)

Expression for the shear viscosity obtained in chapter-3 is given as

\[ \eta^s = \frac{\eta_0}{g(\sigma)} \left[ 1 + \frac{4}{5} \nu + \frac{12}{5 \pi} \nu^2 \right]. \]  
(4.79)

Using the relation among the three viscosities, we obtain

\[ \eta^b = a_B \frac{\eta_0}{g(\sigma)} \nu^2, \]  
(4.80)

where \( a_B = \left[ \frac{4}{\pi} - \frac{4}{15} \right] = 1.0066 \)

The numerical factor \( a_B \) predicted by Enskog is 1.0186. Thus, it is gratifying to see that our method provides the value of the bulk viscosity in close agreement with the Enskog result.

4.4 SUMMARY AND CONCLUSION

In this chapter, we have obtained an expression for the binary collision contribution to the first-order memory function of the longitudinal current correlation function using the cluster expansion technique. This expression involves the static pair correlation function and the time dependence of position, momentum and acceleration of a particle. Our expression has advantageous over the kinetic theory as it can easily be used for any central potential. Thus, the present formalism provides a methodology to
obtain the longitudinal and the bulk stress auto-correlation functions in the binary collision approximation for system of particles of a fluid interacting via continuous potential. The numerical calculations for the continuous interaction potential are feasible due to appearance of position and momentum of a particle moving in a central potential. In the limit of hard sphere, our results for the longitudinal and bulk viscosities are found to be in agreement with the Enskog results.