In this chapter, we have studied the velocity auto-correlation function and the self-diffusion coefficient of Lennard-Jones fluids. The VACF which is a microscopic manifestation of the self-diffusion coefficient is a fundamental quantity in the study of dynamics of a single particle in a condensed many body system. It contains information about the motion of a tagged particle under the influence of all other particles in the system. The binary collision expression for the auto-correlation function of force of a particle, which is related to the memory function of the VACF, has already been derived[59]. The numerical calculations for a fluid of particles interacting via Lennard-Jones fluid have also been done. Since, the numerical results of the force auto-correlation function are known within the binary collision expansion approximation, one can model this correlation function to calculate the VACF and can apply it to any density and temperature of the fluid. In the past, the phenomenological models have mainly been proposed for the memory function. In the present work, we propose a model[70] for the force auto-correlation function. The parameters of the model are determined from the frequency sum rules of the VACF to incorporate exactly its short time behavior. The values of the sum rules and the Green-Kubo expression have been used to determine the self-diffusion
coefficient and results are compared with the available molecular dynamics data. Results of the model for FACF and VACF are compared with binary collision expansion and MD results. This demonstrates the extent up to which the binary collision results are valid for moderate density of the fluid.

5.1 GENERALITIES

For an isotropic fluid, the normalized velocity auto-correlation function $\psi(t)$ is defined as

$$\psi(t) = \frac{\langle v_{ix}(t)v_{ix}(0) \rangle}{\langle v_{ix}^2 \rangle}.$$  \hfill (5.1)

Thus, $\psi(t)$ is a measure of the projection of the particle velocity at time $t$ onto its initial value, averaged over all initial conditions. In Eq.(5.1), $v_{ix}(t)$ is the $x$-component of the velocity of a tagged particle 1 at any time $t$. The time integral of the velocity auto-correlation function is related to the self-diffusion coefficient of the fluid particles. In order to obtain this relation, we consider a set of identical, tagged particles having positions around a point $R(0)$. If the particles diffuse in time $t$ to positions around $R(t)$, the self-diffusion coefficient is given by a well known relation due to Einstein:

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle |R(t) - R(0)|^2 \rangle.$$  \hfill (5.2)

This result is a direct consequence of Fick's law of diffusion. Writing the Einstein relation (5.2) in terms of velocity auto-correlation function, we find that
\[ R(t) - R(0) = \int_0^t dt' \, v(t'). \quad (5.3) \]

Squaring and averaging the above equation over initial conditions, we obtain

\[
\langle |R(t) - R(0)|^2 \rangle = \int_0^t \int_0^t dt' dt'' \langle v(t') \cdot v(t'') \rangle. \quad (5.4)
\]

or

\[
\langle |R(t) - R(0)|^2 \rangle = \int_0^t \int_0^t dt' dt'' \langle v(t' - t'') \cdot v(0) \rangle. \quad (5.5)
\]

Using the properties of symmetry with respect to time inversion and invariance under time translation, the above equation can be combined with definition of the VACF, i.e., Eq.(5.1) to give

\[
\langle |R(t) - R(0)|^2 \rangle = \frac{6k_B T}{m} \int_0^t dt' (t-t') \psi(t'). \quad (5.6)
\]

Substituting Eq.(5.6) in Eq.(5.2), we obtain

\[
D = \frac{k_B T}{m} \int_0^\infty dt \, \psi(t). \quad (5.7)
\]

The upper limit of integration in the above equation is now set equal to infinity to indicate that long time also means a time long compared to any characteristic relaxation time of \( \psi(t) \). This equation is called the Green-Kubo formula for the self-diffusion coefficient and is valid for any density, temperature and generally for any classical system in which the diffusion coefficient is governed by conservation law of mass.

The time evolution of the VACF can be obtained by using the Mori's equation of motion given as
\[ \frac{d\psi(t)}{dt} = - \int_0^t M(t-\tau) \psi(\tau) \, d\tau, \quad (5.8) \]

where, \( M(t) \) is the memory function involving the projection operator \( P \) and is given by

\[ M(t) = \frac{\langle \psi_1(0) \exp[i(1 - P)t] \psi_1(0) \rangle}{\langle \psi_1^2(0) \rangle}. \quad (5.9) \]

Dropping the projection operator \( P \) in the definition of the memory function we obtain an expression for the force auto-correlation function \( F(t) \) which is given as

\[ F(t) = \frac{\langle \psi_1(0) \exp[i(1t)] \psi_1(0) \rangle}{\langle \psi_1^2(0) \rangle} = -\psi(t), \quad (5.10) \]

where, \( \psi(t) \) is the second derivative of \( \psi(t) \) w. r. t. time \( t \). The correlation function \( F(t) \) satisfies its exact properties

\[ \int_0^\infty dt \, F(t) = 0 \quad \text{and} \quad \int_0^\infty dt \, t \, F(t) = -1. \quad (5.11) \]

Differentiating Mori's equation of motion one obtains a relation among VACF, FACF and the memory function given as

\[ M(t) = F(t) - \int_0^t \, d\tau \, M(t-\tau) \, \dot{\psi}(\tau). \quad (5.12) \]

From the above equation, it is clear that for \( t = 0 \), \( M(t) \) and \( F(t) \) are identical. It is also seen that for short times, the behavior of \( M(t) \) and \( F(t) \) can not differ greatly as the contribution from the integral remains small. Therefore, the approximation \( M(t) = F(t) \) could be very effective in representing the essential short time features of \( M(t) \). Taking the Fourier-Laplace transform of Eqs. (5.8) and (5.12), we obtain
\( \tilde{\psi}(\omega) = \frac{\psi(0)}{\omega + \tilde{M}(\omega)} \), \hspace{1cm} (5.13) \\
and \\
\( \tilde{F}(\omega) = -\omega \tilde{\psi}(\omega) \tilde{M}(\omega) \). \hspace{1cm} (5.14)

Eliminating \( \tilde{\psi}(\omega) \) from Eqs. (5.13) and (5.14), we obtain a relation between memory function and FACF in \( \omega \)-space given as

\[
\tilde{M}(\omega) = \frac{\omega \tilde{F}(\omega)}{\omega - \tilde{F}(\omega)} .
\] \hspace{1cm} (5.15)

Writing

\[
\tilde{F}(\omega) = F'(\omega) + iF''(\omega)
\] \hspace{1cm} (5.16)

where \( F'(\omega) \) and \( F''(\omega) \) represent, respectively, the real and imaginary parts of \( \tilde{F}(\omega) \), we obtain expressions for the real and imaginary parts of \( \tilde{M}(\omega) \), given as

\[
M'(\omega) = \frac{\omega^2 F'(\omega) - \omega[F'^2(\omega) + F''^2(\omega)]}{[\omega - F'(\omega)]^2 + F''^2(\omega)}
\] \hspace{1cm} (5.17a)

and

\[
M''(\omega) = \frac{\omega^2 F''(\omega)}{[\omega - F'(\omega)]^2 + F''^2(\omega)}.
\] \hspace{1cm} (5.17b)

The memory function in time domain is readily obtained from the following expression:

\[
M(t) = \frac{2}{\pi} \int_{0}^{\infty} \cos(\omega t) \tilde{M}''(\omega) \, d\omega .
\] \hspace{1cm} (5.18)

Defining the frequency spectrum \( f(\omega) \) of the VACF as

\[
f(\omega) = 2 \psi''(\omega) = 2 \int_{0}^{\infty} \cos(\omega t) \psi(t) \, dt ,
\] \hspace{1cm} (5.19)

where \( \psi''(\omega) \) is the imaginary part of \( \tilde{\psi}(\omega) \). The expression for \( \psi''(\omega) \) is obtained from Eq. (5.13) by writing \( \tilde{M}(\omega) = M'(\omega) + iM''(\omega) \)

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and is given by
\[
\psi'(\omega) = \frac{M''(\omega)}{\left[\omega + M'(\omega)\right]^2 + \left[M'(\omega)\right]^2}.
\] (5.20)

The time evolution of \( \psi(t) \) can be obtained from
\[
\psi(t) = \frac{1}{\pi} \int_0^\infty \cos(\omega t) f(\omega) \, d\omega.
\] (5.21)

Expression for the self-diffusion coefficient obtained from Eqs. (5.7), (5.19) and (5.20) is given as
\[
D = \frac{k_B T}{m} \frac{\psi''(0)}{\psi'(0)} = \frac{k_B T}{m} \left[ M'(0) \right]^{-1}.
\] (5.22)

5.2 BINARY COLLISION CONTRIBUTION TO THE FORCE AUTO-CORRELATION FUNCTION

The microscopic expression for the force auto-correlation function obtained by Pathak et al[59] within the binary collision approximation is given as
\[
F_{\langle t \rangle} = \frac{n}{2\sqrt{2m}} \iint dr \, dp \, G\left(\frac{p}{\sqrt{2}}\right) \frac{\partial g(r)}{\partial x} F_x(r(t)),
\] (5.23)
where, \( g(r) \) and \( G(p) \) are the pair distribution function and Maxwellian momentum distribution function, respectively. In the above equation, the position and momentum vectors of the particle moving in a central potential \( u(r) \) are determined from the equation of motion given as
\[
F_x = -\frac{\partial u(r)}{\partial x} = \frac{1}{2} \frac{dp_x}{dt} = \frac{m}{2} \frac{d^2x}{dt^2}.
\] (5.24)

Eq.(5.23) contains effects of all uncorrelated binary collisions and the density dependence is more complicated because of the appearance
of derivative of $g(r)$. The numerical calculations of $F(t)$ for Lennard-Jones fluids had been made for various densities and temperatures. Results obtained for $F(t)$ and $\psi(t)$ were compared with the MD data and found to agree with the MD data for densities and temperatures where it was expected. The comparison suggests that the inclusion of multiparticle or long time effects is needed at densities and temperatures close to the triple point. This can be included by performing mode-coupling calculations. In the past, the binary collision part as mentioned earlier was generally been replaced by a phenomenological form. Since, now we know its microscopic results, one can develop better models to represent binary collision contribution. In the next section, we propose a two parameter model for the force auto-correlation function.

### 5.3 A MODEL FOR THE FORCE AUTO-CORRELATION FUNCTION

The phenomenological forms for $M(t)$ or $F(t)$ can be introduced to preserve number of properties of the velocity auto-correlation function. There exist many works[18,19,40] in the literature in which phenomenological form for the memory function has been proposed to study the time evolution of TCFs. But, till now there exist only few studies in which one approximates the FACF to calculate the VACF. In the present work, we propose a phenomenological form for the force auto-correlation function $F(t)$ given as

$$F(t) = F(0) \exp(-\beta t^2) \cos(bt), \quad (5.25)$$

with its short time expansion:
\[ F(t) = F(0) \left[ 1 - \frac{t^2}{2} (b^2 + 2\beta) + \ldots \right] . \] (5.26)

Taking the Fourier-Laplace transform of Eq. (5.26) and separating real and imaginary parts, we have[71]

\[
F'(\omega) = -\frac{1}{2} \left[ \frac{(\omega + b)^2}{2\beta} \sum_{K=1}^{\infty} \frac{1}{(2K-1)!} \left\{ \frac{-(\omega + b)^2}{2\beta} \right\}^{K-1} \right]
+ \frac{(\omega - b)}{2\beta} \sum_{K=1}^{\infty} \frac{1}{(2K-1)!} \left\{ \frac{-(\omega - b)^2}{2\beta} \right\}^{K-1} .
\] (5.27)

\[
F''(\omega) = \frac{1}{4} \sqrt{\frac{\pi}{\beta}} \left[ \exp -\frac{(\omega - b)^2}{4\beta} + \exp -\frac{(\omega - b)^2}{4\beta} \right].
\] (5.28)

Two parameters of Eq.(5.25) are obtained by comparing Eq.(5.26) with the short time expansion of \( F(t) \) given as

\[
F(t) = V_2 \left[ 1 - \frac{t^2}{2!} \frac{V_4}{V_2} + \ldots \right] ,
\] (5.29)

we obtain

\[
F(0) = V_2
\] (5.30a)

and

\[
b^2 + 2\beta = V_4/V_2 .
\] (5.30b)

In the above equation, \( V_2 \) and \( V_4 \) are the second and the fourth frequency rules of the VACF, respectively. The explicit egressions[72] for these are given as

\[
V_2 = \frac{4\pi n}{3} \int_0^\infty dr g(r) r^2 (3B + Ac^2)
\] (5.31)

and

\[
V_4 = \frac{8\pi n}{3m} \int_0^\infty dr g(r) r^2 (3B^2 + A^2c^4 + ABc^2)
\]
where \( n, T \) and \( m \) are the density, temperature and atomic mass, respectively and \( g_3(r,r_1) \) is the triplet correlation function. In Eqs.(5.31) and (5.32), we have introduced the following notations:

\[
A = \frac{1}{r} \frac{\partial B}{\partial r}, \quad B = \frac{1}{r} \frac{\partial u(r)}{\partial r}
\]

and \( \beta \) is the cosine of the angle between \( r \) and \( r_1 \). The subscript 1 on \( A \) and \( B \) implies that the argument of the potential is changed to \( r_1 \).

Further, we assume that the FACF oscillates with Einstein frequency equal to \( \sqrt{V_2} \). This sets one of the parameters of \( F(t) \), i.e.,

\[
b^2 = V_2,
\]

and hence

\[
\beta = \frac{1}{2} \left( \frac{V_4}{V_2} - V_2 \right). \quad (5.33b)
\]

Since, our model does not satisfy its exact properties, i.e., Eq.(5.11), it yields unphysical result for the self-diffusion coefficient obtained by using Eqs.(5.17) and (5.22). Therefore, we assume[59] that \( M(t) = F(t) \) for all times and hence obtain an expression for the self-diffusion coefficient given by

\[
D = \frac{k_B T}{m} \left[ F'(0) \right]^{-1}
\]
In the next section, we use this expression to calculate the self-diffusion coefficient.

5.4 RESULTS AND DISCUSSION

In order to calculate the self-diffusion coefficient from Eq. (5.34), we require $V_2$ and $V_4$ as inputs. General expressions for these are given by Eqs. (5.31) and (5.32), respectively. The calculation of $V_2$ involves only the static pair correlation function whereas $V_4$ involves both static pair and triplet correlation functions along with the interatomic potential. Due to limited information about the static triplet correlation function, the superposition approximation has been used. The validity of the superposition approximation has been checked in the work of Tankeshwar, Pathak and Ranganathan[40]. It was noted that the use of superposition approximation does not introduce significance error in the calculation of the sum rules. In the present work, we have used the results of Tankeshwar et al[72] for the sum rules to calculate the self-diffusion coefficient of LJ fluids using Eq. (5.34). Results obtained for the self-diffusion coefficient $D^* = D \left( \frac{m}{\epsilon \sigma} \right)^{1/2}$, where $\sigma$ and $\epsilon$ are two parameters of LJ fluids, are plotted in Figure (5.1) as a function of density, $n^*( = n \sigma^3)$, for six isotherms. The molecular dynamics results of Heyes[73] are also shown there. The temperature dependence of the self-diffusion coefficient is presented in Figure (5.2) for six densities along with the computer
Fig. 5.1 Variation of $D^*.n^*$ with reduced density $n^*$ at various temperatures. Solid lines represent our results. MD results are shown as symbols.
Fig. 5.2 Variation of the self-diffusion coefficients with temperature. Solid lines are our results. MD results are shown as symbols.
It can be seen from Figures (5.1) and (5.2) that a good agreement is obtained at temperature above the critical temperature and densities below the triple point density. Results of the self-diffusion coefficient at the triple point are almost twice as that of the computer simulation data. This is an expected result as our model does not satisfy the properties of the FACF given by Eq. (5.11) and further, the approximation $M(t) = F(t)$ is valid only at short times. Thus, our model does not include the correct intermediate and long time behaviors of $\psi(t)$ which play an important role in determining the self-diffusion coefficient of dense fluids. Here, it may be pointed out that our purpose of proposing a model was to represent the binary collision contribution and not to determine the self-diffusion coefficient of dense gases and liquids.

It is of interest to see the behavior of $M(t)$ obtained from Eqs. (5.17) and (5.18). Since we expect good results only for the low density fluid, results obtained for $M(t)$ at the lowest density investigated here are shown as solid circles in Figure (5.3). Corresponding simulation results of $M(t)$ are also shown there as a continuous line. It can be seen from Figure (5.3) that the model calculation provides $K(0) \neq F(0)$ which has also been noted by Pathak et al [59]. However, our model predicts a reasonable agreement with the simulation results at large times.

It is also of interest to compare our results for the FACF with its binary collision approximation. In Figures (5.4a) and (5.4b), we have compared the results obtained by Pathak et al [59] for the FACF within the binary collision approximation with those obtained from
Fig. 5.3 Variation of memory function $M(t)/V_2$ with time $t^* = t(e/m\sigma)^{1/2}$. Full circles are our results whereas solid line represent molecular dynamics data[74].
Fig. 5.4(a) Variation of the normalized FACF $F(t)$ with time $t^* = \left(\frac{t \sigma}{48 \mu c/mc} \right)^{1/2}$ for $T^* = 0.73$ and $n^* = 0.84$. Dotted line is the result of our model whereas, plus signs represent results of Ref.[59] and diamonds represent MD data.

Fig. 5.4(b) Same as Fig. 5.4(a) but for $T^* = 2.5$ and $n^* = 0.4$. Dotted line is our results and diamonds represent results of Ref.[59].
our proposed model for two thermodynamic states. Dotted line is results of our model whereas diamonds represent MD results\[73\]. The plus signs in Figure (5.4a) represent results obtained within the binary collision approximation. It is noted that, for short times, the results of our model and that of binary collision expansion method for the FACF are in reasonable agreement with those obtained by computer simulation.

We calculate the time evolution of $\psi(t)$ from Eq. (5.21) using $M(t) = F(t)$ in Eq. (5.20). Results thus obtained are shown as dotted and continuous curves in Figure (5.5a) and (5.5b), respectively, for five thermodynamic states. Simulation results of Kushick and Berne\[74\] and of Lee and Chung\[75\] are also shown there as diamonds and solid circles, respectively. In Figure (5.5a), results obtained for $\psi(t)$ within the binary collision approximation are also shown there as plus signs. This demonstrates the extent upto which the binary collision results are valid. From Figure (5.5a) and (5.5b), it is seen that our model reproduces the short time behavior of the VACF. At intermediate and long times good agreement of results of our model and that of binary collision expansion method with the MD data is obtained only at the lowest density investigated here. This is consistent with our finding of the self-diffusion coefficient. Thus, our model could represent only a binary collision part of the FACF.

**SUMMARY AND CONCLUSION**

In this chapter, we have studied the dynamics of a tagged
Fig. 5.5(a). Variation of the normalized VACF $\psi(t)$ with time $t^* = t(4\sigma/m\sigma)^{1/2}$. Dotted line is the results of our model whereas diamonds represent MD results and plus signs are the results of Ref.[59].
Circles represent MD data. Solid line is the results of our model whereas full temperature. Solid line is the results of our model whereas full.

Fig. 5(b) same as Fig. 5(a) but for different densities and

\[ \tau = 7.64 \]
\[ u = 0.85 \]

\[ \tau = 5.064 \]
\[ u = 0.65 \]

\[ \tau = 1.84 \]
\[ u = 0.75 \]
particle and calculated the self-diffusion coefficient using a simple model for the FACF. It is found that results obtained for the self-diffusion coefficients are in agreement with computer simulation data for a fluid range away from the triple point. The disagreement near the triple point may be due to the fact that our proposed model for the FACF could represent only the binary part and therefore, can be valid only in the low density limit. The study presented here is expected to be useful in further modeling the FACF and in the studies where the binary collision contribution to the memory function is replaced by a phenomenological function and multiparticle dynamics is taken care by mode-coupling calculations.