IC/93/208

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

ANALYTICAL SOLUTION OF MORI'S EQUATION WITH SECANT HYPERBOLIC MEMORY

K. Tankeshwar

and

K.N. Pathak

INTERNATIONAL ATOMIC ENERGY AGENCY

UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

MIRAMARE-TRIESTE

IC/93/208

International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

ANALYTICAL SOLUTION OF MORI'S EQUATION WITH SECANT HYPERBOLIC MEMORY

K. Tankeshwar *
International Centre for Theoretical Physics, Trieste, Italy
and
K.N. Pathak
Centre of Advanced Study in Physics, Department of Physics,
Panjab University, Chandigarh 160014, India.

ABSTRACT

The equation of motion of the auto–correlation function has been solved analytically using a secant–hyperbolic form of the memory function. The analytical results obtained for the long time expansion together with the short time expansion provide a good description over the whole time domain as judged by their comparison with the numerical solution of Mori's equation of motion. We also find that the time evolution of the auto–correlation function is determined by a single parameter τ which is related to the frequency sum rules up to the fourth order. The auto–correlation function has been found to show simple decaying or oscillatory behaviour depending on whether the parameter τ is greater than or less than some critical values. Similarities as well as differences in time evolution of the auto–correlation have been discussed for exponential, secant–hyperbolic and gaussian approaches of the memory function.

MIRAMARE – TRIESTE
July 1993

* Permanent address: Centre of Advanced Study in Physics, Department of Physics, Panjab University, Chandigarh 160014, India.

1 INTRODUCTION

A considerable amount of work has been done in recent years for the study of time evolution of the auto-correlation functions (ACFs) and the transport coefficients of atomic fluids. In these studies, equilibrium [1,2] and non-equilibrium molecular dynamics[3-6] techniques have been used to investigate the velocity, stress and energy current density auto-correlation functions. On the other hand, theoretical study of the ACFs can be made[7] through Mori's integro differential equation. In this approach, the fundamental theoretical quantity to be calculated is the memory function. The reduction of the problem of studying the ACFs to calculate the appropriate memory function is a an important step in the theoretical analysis of atomic motion in fluids. Since the exact microscopic calcultion of the memory function is not yet feasible, in general, simple approximations to the memory function can be made which preserve the number of important properties of ACF irrespective of the approximation introduced for the memory function. In the present work, we use a secant-hyperbolic form of the memory function, which is a solution of a non-linear differential equation well known in soliton dynamics. This memory function has been used by us[8-11] and also by Heyes and Powels[12] in the study of time correlation functions (TCFs) and transport coefficients of classical dense fluids and has provided a very satisfactory agreement with the available computer simulation data. In fact, very recently Leegwater[13] has derived an expression for the first order memory function of the velocity auto-correlation function using the kinetic theory approximation which is identical to the secant-hyperbolic memory. But in all the earlier studies of the time correlation function using secant-hyperbolic memory, the underlying Mori equation has been solved only numerically. Therefore, the aim of the present study is to solve analytically the Mori equation with secant-hyperbolic memory. The analytical solutions provide a clearer picture of the time evolution of the ACFs as has also been demonstrated by Denner and Wagner [14] using an exponential and a gaussian memory function.

The layout of the paper will be as follows. In Section 2 we introduce the mei ory function used in this work. In section 3, we discuss the Fourier spectrum of the ACF. The analytical short and long time expansions for the ACF are obtained in section 4. Section 5 contains an analytical investigation of the poles of the Laplace transform of the ACF. The validity of analytical expressions for the poles is also checked in this section by comparing with numerical results. In section 6, we compare our analytical results with one obtained from numerical calculation of the ACF. In section 7, the results of ACF due to secant-hyperbolic memory are compared with that due to gausssian and exponential memory.

2 THE MODEL MEMORY FUNCTION

Mori has shown that ACFs obey an equation of motion [8] which determines their time evolution. It is given by

$$\frac{dC(t)}{dt} + \int_0^t C(t')M_1(t-t')dt' = 0 \tag{1}$$

where C(t) is the ACF of some dynamical variable A(t). $M_1(t)$ is the first order memory function and is defined as

$$M_1(t) = < f_1(t) f_1^*(0) > / < |f_1(0)|^2 > \qquad (2)$$

where,

$$f_1(t) = exp(iQ_1LQ_1t)Q_1A.$$

The operator $Q_1(= 1 - P_1)$ projects onto the subspace orthogonal to the variable A(t). The angular brackets in Eq.(2) represent the ensemble average and L is Liouville operator. In order to calculate time evolution of the ACF from Eq.(1), the fundamental theoretical quantity needed is the memory function $M_1(t)$. If we apply the projection operator technique used in deriving Eq.(1) to the case when $f_1(t)$ is treated as the dynamical variable, we obtain an equation similar to Eq.(1) for the time evolution of the $M_1(t)$. This provides

$$\frac{dM_1(t)}{dt} = \int_0^t M_1(t')M_2(t-t')dt' = 0 \qquad (3)$$

where, $M_2(t)$ is second order memory function defined as

$$M_2(t) = < f_2(t) f_2^*(0) > / < |f_2(0)|^2 > \qquad (4)$$

with

$$f_2(t) = exp(iQ_2LQ_2L)Q_2f_1,$$

$$Q_2 = 1 - P_1 - P_2$$

and the operator P_2 projects on ordinary dynamical variable $f_1(t)$. We differentiate Eq.(3) w.r.t. time t to obtain

$$\frac{d^2M_1(t)}{dt^2} + b^2M_1(t) + \int_0^t \frac{dM_2(t-t')}{dt} M_1(t')dt' = 0 \qquad (5)$$

where $M_2(0) = b^2 = \delta_2 = (C_4/C_2 - C_2)$ with C_{2n} being the nth order sum rule of the ACF. Now the problem of calculating time development of the ACF reduces to the calculation of $M_2(t)$ or $M_1(t)$ which themselves are the time correlation functions of time derivatives of the original dynamical variable A(t). The exact microscopic calculation of $M_1(t)$ or $M_2(t)$ is not yet possible. Therefore, several phenomenological forms of the memory function have been proposed in the literature [8-12]. In this work we take

$$M_1(t) = a sech(bt) \qquad (6)$$

with $a = M_1(0) = \delta_1 = C_2$. This memory function tends to Gaussian and a simple exponential for the short and long times, respectively. It is also noted that $M_1(t)$ given by Eq.(6) is a solution of a non-linear differential equation, well known in soliton dynamics, given by

$$\frac{d^2M_1(t)}{dt^2} - b^2M_1(t) + \frac{2b^2}{a^2}M_1^3(t) = 0. \qquad (7)$$

The analytical results obtained for the time correlation function using the secant-hyperbolic memory function is expected to demonstrate the effect of the non-linearity reflected through Eq.(7) of the atomic motion on the time evolution of ACF.

3 POWER SPECTRUM OF THE AUTO CORRELATION FUNCTION

In order to calculate the time evolution of the ACF, C(t) and its power spectrum we rewrite Eq.(1) as

$$\frac{dC(\hat{t})}{d\hat{t}} + \frac{2}{\pi\tau}\int_0^t sech(\xi)C(\hat{t}-\xi)d\xi = 0 \qquad (8)$$

where, the reduced time scale is $\hat{t} = \sqrt{\delta_2}t$ and

$$\tau = (2/\pi)(\delta_2/\delta_1). \qquad (9)$$

In Eq.(8) we have used the memory function as given by Eq.(6). It may be noted that now the ACF involves only one essential parameter τ. Defining the Laplace transform as

$$\tilde{C}(z) = \int_0^\infty exp(-z\hat{t})C(\hat{t})d\hat{t}, \qquad (10)$$

we obtain

$$\tilde{C}(z) = \frac{1}{z + \frac{2}{\pi\tau}\beta(\frac{z+1}{2})} \qquad (11)$$

where

$$\beta(\frac{z+1}{2}) = \int_0^\infty sech(\hat{t})exp(-\hat{t}z)dt$$

and has the series expansion [15]

$$\beta(x) = \sum_{k=0}^\infty \frac{(-1)^k}{x+k}. \qquad (12)$$

The Fourier transform $G(\omega)$ of the ACF, $C(t)$ is related to its Laplace transform $\tilde{C}(z)$ as

$$G(\omega) = \frac{1}{2\pi}\int_{-\infty}^\infty d\hat{t}exp(-i\omega\hat{t})C(\hat{t}) = \frac{1}{\pi}Re\tilde{C}(\omega)) \qquad (13)$$

Inserting Eq.(11) in Eq.(13), the power spectrum $G(\omega)$ is obtained as

$$G(\omega) = \frac{\tau}{\pi}\frac{sech[\frac{\pi\omega}{2}]}{(\omega\tau + F(\omega))^2 + sech^2[\frac{\pi\omega}{2}]}, \qquad (14)$$

where

$$F(\omega) = \frac{\pi}{2}tanh[\frac{\pi\omega}{2}] + \frac{1}{2}[\psi(\frac{1+i\omega}{4}) - \psi(\frac{1-i\omega}{4})]. \qquad (15)$$

In above equation, $\psi(x)$ is Euler Psi function. We note that $F(\omega)$ has the expansions

$$F(\omega) = \frac{\omega}{4}[\pi^2 - \sum_{k=0}^\infty[\frac{1}{4}+k]^2] - [\frac{\pi\omega}{2}]^3\frac{\pi}{6}......, \qquad (16)$$

for small ω and

$$= \frac{\pi}{2} - \frac{-1}{2}\sum_{k=0}^{\infty}\frac{1}{\frac{\omega}{4} + \frac{[\frac{1}{2}+k]^2}{\omega}4} \quad (17)$$

for large ω. Using Eq.(16) and the series expansion of $sech(\pi\omega/2)$, we obtain the low frequency behaviour of $G(\omega)$ as

$$G(\omega) = \frac{\tau}{\pi}[1 + \frac{\pi^2}{8}\omega^2(1 - 2[\frac{2}{\pi}\tau + 1 - \frac{16}{\pi^2}]^2)] \quad (18)$$

However for large ω

$$G(\omega) = \frac{\tau}{\pi}\frac{sech[\frac{\pi\omega}{2}]}{\tau^2\omega^2} \quad (19)$$

It is evident from Eqs.(18) and (19) that $G(\omega)$ will have a maximum for $\tau < \tau_m = \frac{\pi}{2}[\frac{1}{\sqrt{2}} - 1 + \frac{16}{\pi^2}]^2 \approx 2.1$. In Fig.(1), the power spectrum $G(\omega)$ of the ACF is shown over the entire frequency range for different values of τ. Following Denner and Wagner [14], we also find that the maximum in the power spectrum for $w > 0$ constitutes a sufficient condition for oscillatory decay of the ACF. In the next section it is shown that for oscillatory behaviour of C(t) is observed even for values $\tau > \tau_m$. This implies that the oscillatory behaviour of C(t) is not a necessary condition for the existence of non-zero ω peak in $G(\omega)$.

4 SHORT AND LONG TIME EXPANSION FOR THE AUTO CORRELATION FUNCTION

The time evolution of C(t) can be obtained by taking the inverse Laplace transform of Eq.(11) i.e,

$$C(\hat{t}) = \frac{1}{2\pi i}\int_{-i\infty}^{+i\infty} dz exp(z\hat{t})\tilde{C}(z). \quad (20)$$

The short time expansion of $C(\hat{t})$ is given by

$$C(\hat{t}) = 1 - \frac{2}{\pi\tau}\frac{t^2}{2} + O(t^4). \quad (21)$$

On the other hand, long time expansion of $C(\hat{t})$ is determined by evaluating the poles of $\tilde{C}(z)$ which are close to zero. In the next section, it is shown that there are two poles z_1 and z_2 in this region. The remaining poles give rise to terms which decay much faster. In view of the above fact and following the procedure of Denner and Wagner [14], we obtain long time expansion of Eq.(20) as

$$\frac{1}{2\pi i}\int_{-i\infty}^{+i\infty} dz exp(z\hat{t})\tilde{C}(z) = \frac{exp(z_1\hat{t})}{1 + \frac{1}{\pi\tau}\beta'(\frac{z+1}{2})|_{z=z_1}} + \frac{exp(z_2\hat{t})}{1 + \frac{1}{\pi\tau}\beta'(\frac{z+1}{2})|_{z=z_2}}, \quad (22)$$

where $\beta'(\frac{z+1}{2})$ is first derivative of $\beta(\frac{z+1}{2})$ w.r.t z. This expansion is useful only if the poles z_1 and z_2 are known.

5 INVESTIGATIONS OF THE POLES

5.1 General Properties of the Poles

The poles of $\tilde{C}(z)$ are given by the solution of the equation

$$f(z) = z + \frac{2}{\pi\tau}\beta(\frac{z+1}{2}) = 0. \quad (23)$$

In order to obtain the properties of the poles , we have solved Eq.(23) graphically for real z (=x) as shown in Fig. (2). We observe the following. (i) Positive real axis is free of poles, (ii) for $\tau > \tau_c$ there exist two poles near the origin on the negative real z axis, (iii) for $\tau = \tau_c$ both the poles coincide and (iv) for $\tau < \tau_c$ there exists no pole on real axis. One can easily see from Eq.(22) that for $\tau < \tau_c$, poles being in the complex z plane, ACF shows oscillatory behaviour. For $\tau = \tau_c$ we have $z_1 = z_2 = x_c$ and obtain the conditions

$$f(x_c) = 0 \Rightarrow -\tau_c x_c = \frac{2}{\pi}\beta(\frac{x_c+1}{2}) \quad (24a)$$

and

$$f'(x_c) = 0 \Rightarrow -\tau_c = \frac{1}{\pi}\beta'(\frac{x_c+1}{2}). \quad (24b)$$

From Eq.(24a) and (24b), we find

$$x_c\beta'(\frac{x_c+1}{2}) = 2\beta(\frac{x_c+1}{2}). \quad (25)$$

This equation can be solved numerically for x_c and hence for τ_c. We find $x_c = -0.47139$ and $\tau_c = 4.4$. It may be noted that τ is an independent parameter and is related to the frequency sum rules whereas, z_1 and z_2 vary with τ. In order to have analytical dependence of z on τ we consider different regions of τ.

5.1.1 $\tau >> \tau_c$

From Fig.(2), it can be seen that

$$\lim_{\tau\to\infty} z_1(\tau) = 0 \quad (26)$$

and

$$\lim_{\tau\to\infty} z_2(\tau) = -1. \quad (27)$$

Therefore, poles $z_1(\tau)$ may be obtained by expanding f(z) around z=0 up to terms of order z^2. The expression thus obtained is given as

$$z_1(\tau) = \frac{-\tau_1\pi}{\beta''(1/2)}[1 - [1 - \frac{2\beta'(1/2)}{\pi\tau_1^2}]^{1/2}] \quad (28)$$

where $\tau_1 = \tau + \frac{1}{2}\beta''(1/2)$. On the other hand, the pole $z_2(\tau)$ is obtained by using expression (12) in Eq.(23).

$$z_2(\tau) = -\frac{1}{2} - \frac{1}{2}[1 - \frac{16}{\pi\tau}]^{1/2}. \quad (29)$$

For very large values of τ, the contribution of pole $z_2(\approx -1)$ to ACF is negligible as seen from the expression (22) whereas, $z_1(\tau) = -1/\tau$ for $\tau \to \infty$ is the leading term in Eq.(28). The resulting long time expansion is given as

$$C(\hat{t}) = exp(-\hat{t}/\tau). \tag{30}$$

Thus, for very large values of τ the ACF, C(t) decays with a time constant τ. This result corresponds to $M_1(t) = \frac{1}{\tau}\delta(t)$ and agrees with that obtained from Eq.(1).

5.1.2 $\tau \geq \tau_c$

For $\tau = \tau_c$ we have $z_1(\tau_c) = z_2(\tau_c) = x_c$. Therefore, for slightly larger values of $\tau(\geq \tau_c)$, z_1 and z_2 can be derived from the series expansion of f(z) around $x = x_c$. Using the relations (24a) and (24b), the expressions for z_1 and z_2 are derived to be

$$z_1 = x_c - \frac{2\tilde{\tau}}{K}[1 - (1 - \frac{Kx_c}{\tilde{\tau}})^{1/2}] \tag{31}$$

$$z_2 = x_c - \frac{2\tilde{\tau}}{K}[1 + (1 + \frac{Kx_c}{\tilde{\tau}})^{1/2}] \tag{32}$$

with $\tilde{\tau} = \tau - \tau_c$ and $K = (1/\pi)\beta''(\frac{x_c+1}{2})$.

5.1.3 $\tau \leq \tau_c$

For $\tau \leq \tau_c$ there exists no pole on the real axis. Taking the complex conjugate of Eq.(23) and noting $\beta(\frac{z^*+1}{2}) = [\beta(\frac{z+1}{2})]^*$, we see that the poles are always complex conjugate to each other. This condition is necessary for C(t) to be real. As a result of the complex nature of the poles, oscillations occur in C(t). Thus τ_c separates the region of the oscillatory behaviour from that of monotonic decay of ACF. The investigation of region $\tau \leq \tau_c$ involves a more detailed analysis which has been given in the appendix. There, we have obtained the approximate expressions for the poles $z_{1,2}(\tau) = x(\tau) \pm iy(\tau)$ with

$$x(\tau) = \frac{\tau_{cc}}{2} + \frac{\tau - \tau_c}{\tau K'} \tag{33}$$

and

$$y(\tau) = [\frac{24\pi(\tau - \tau_c)}{\beta'''(\frac{x_c+1}{2})}]^{1/2} \tag{34}$$

where $K' = \beta'''[\frac{x_c+1}{2}]/6\beta'[\frac{x_c+1}{2}]$.

For a more accurate description of the poles one needs to solve the following differential equation obtained from Eq.(23)

$$\frac{dz(\tau)}{d\tau} = -\frac{z\tau}{\tau + \frac{1}{\pi}\beta'(\frac{z+1}{2})} \tag{35}$$

with $z = x + iy$.

5.1.4 $\tau \to 0$

In this region the poles tend to the imaginary axis and ACFs shows more oscillations. An analysis of this regime is also given in the appendix. Results are given as

$$x(\tau) = -\frac{1}{\tau}sech(\frac{\pi}{2\tau}) \tag{36}$$

and

$$y(\tau) = -\frac{1}{\tau}. \tag{37}$$

In the next sub section, we check the validity of the above approximate expressions for the poles of $\tilde{C}(z)$.

5.2 Estimation of Validity

The validity of various analytical formulae derived in previous sub-section is checked by solving Eq.(23) numerically for z_1 and z_2. These numerically determined z_1 and z_2 along with their corresponding analytical values are shown in Fig.(3a) and Fig.(3b). From Fig.(3a) it can be seen that Eqs.(28) and (31) represent $z_1(\tau)$ very well. However, the pole $z_2(\tau)$ is not well described in the intermediate region $5 < \tau < 7$ by the analytical expressions (29) and (32). For this region , one may have to consider higher order terms in the expansion. For $\tau < \tau_c$, we find that $x(\tau)$ and $y(\tau)$ are very well predicted by Eqs.(33),(36) and (34),(37), respectively. On the whole, we find that our analytical expressions for the poles of $\tilde{C}(z)$ agree well with those obtained by numerical solution of Eq.(23) and therefore, can be used to predict the long time behaviour of the ACF using Eq.(22).

6 COMPARISON BETWEEN NUMERICAL AND ANALYTICAL RESULTS OF C(t)

The equation of motion (Eq.(8)) for the time evolution of the ACF can be solved numerically by taking the inverse Fourier transform of the power spectrum $G(\omega)$ i.e,

$$C(\hat{t}) = \frac{2}{\pi}\int_0^\infty G(\omega)cos(\omega\hat{t})d\omega. \tag{38}$$

The results obtained from Eq.(38) for C($\hat{t}$) are shown as full line in Fig.(4) for different values of τ. The results obtained from the long time expansion (Eq.(22)) have also been shown in Fig.(4) as solid circles. It can be seen from Fig.(4) that our analytical results give an overall good description of $C(\hat{t})$ if one excludes extremely short times. For short time region, the expansion (21) is applicable. Thus, both the expansions taken together yield a good description of the time evolution of ACF in whole time domain for a wide range of parameter τ.

7 COMPARISON AMONG SECH(t), GAUSSIAN AND EXPONENTIAL MEMORY FUNCTIONS

We compare the results of C(t) obtained by using sech(t), a simple exponential and a Gaussian form of the memory function. It is found that common features of ACF discussed by Denner and Wagner [14] for exponential and Gaussian memory are also exhibited by sech(t) memory. These features are summarized as follows. There exist two poles z_1 and z_2 which determine the long time behaviour of the auto-correlation function. For all the three memory functions, there exists a critical value of the parameter τ_c which separates the regime of oscillatory behaviour from that of monotonic decay of the ACF. For $\tau \to \infty$, one of the poles tends to zero and this dominates the long time behaviour of the ACF. However, there are differences among sech(t), exponential and Gaussian memories. These are the following. The poles $Re z_{1,2}$ vary with τ for $\tau < \tau_c$ for Gaussian and secant-hyperbolic memories whereas, these have a fixed value of -0.5 for the exponential memory. On the other hand, for increasing $\tau > \tau_c$ the pole $z_2(\tau)$ approaches -1 for both exponential and sech(t) memories, whereas it tends to $-\infty$ for Gaussian memory. It is also found that the poles show symmetry around z =-0.5 for exponential memory whereas, this kind of symmetry is totally absent in case of gaussian memory. On the other hand, the poles are more or less symmetric for the secant-hyperbolic memory. Thus, the secant hyperbolic model memory function has some common featureswith gaussian and some with the exponential memory.

In order to see the difference in the behaviour of the time evolution of the correlation function using different memory function we have plotted C(t) for exponential, gaussian and sech(t) memories in Fig.(5) for $\delta_2/\delta_1 = \pi$. It can be seen from Fig.(5) that the decay of $C(\hat{t})$ with exponential and guassian memories is slower than in case of sech(t) memory. It is also find that $C(\hat{t})$ attains a negative minima (back scattering effect) for $\hat{t} \approx 7.5$ for secant-hyperbolic memory whereas, it remains positive for the gaussian and exponential memory functions. The above differences in these different cases can be understood by noting that $\tau = \frac{\delta_2}{\delta_1}$ and $\tau_c = 4$, $\tau = \frac{2}{\sqrt{\pi}}\frac{\delta_2}{\delta_1}$ and $\tau_c = 3.811$ and $\tau = \frac{2}{\pi}\frac{\delta_2}{\delta_1}$ and $\tau_c = 4.4$ for exponential, gaussian and secant-hyperbolic memory, respectively. Here τ_c separates the regime of oscillatory behaviour of C(t) from its monotonic decay. From this we find that C(t) will show oscillatory behaviour for $\frac{\delta_2}{\delta_1} < 4, 3.37$ and 6.711 for exponential, gaussian and sech(t) memory functions, respectively. Therefore, it is seen that the back scattering effects are more pronounced for secant hyperbolic memory than for the gaussian and the exponential memories. Thus, our secant hyperbolic memory function reflects more non-linearity which arises due to effect of surrounding on the atomic motion in a dense media. Similarly, for the the power spectrum $G(\omega)$ of C(t), we find that non-zero ω peak appears for sech(t) memory when $\frac{\delta_2}{\delta_1} < 3.27$ whereas, it appears when $\frac{\delta_2}{\delta_1} < 1.887$ for gaussian case. The parameter τ or the sum rules up to fourth order of almost all the ACFs are known [11,16]. Therefore, our study is expected to be quite useful as one now can obtain the information about the nature of the decay of ACF just by knowing the value of parameter and without actually solving the Mori equation numerically.

8 CONCLUSION

In this paper we have obtained an analytical solution of Mori's integro-differetial equation for the ACF using a secant-hyperbolic form of the memory function. We find that long time expansion (22) together with short time expansion (21) provides a good description of C(t) for whole time domain. We have found that the behaviour of ACF depends on a single parameter τ which determines whether ACF decays in an oscillatory or non-oscillatory fashion. This parameter τ is related to the frequency sum rules of the ACF upto the fourth order. Similarities as well as differences in time evolution of C(t) have been discussed for exponential, secant-hyperbolic and gaussian approaches for the memory function. It is found that the back scattering effects are more pronounced in our sech(t) memory than in the gaussian and exponential memory functions. This implies that our model reflects more non-linearity which arises due to the effect of the motion of molecule on its surrounding in a dense media and its reflection on the motion of the molecule.

Acknowledgements

This work was developed at Chandigarh, India and finalized at ICTP,Trieste, Italy. One of us (KT) would like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics during the condensed matter workshop 1993. KT also gratefully acknowledges the partial financial assistance provided by C.S.I.R., New Delhi.

APPENDIX

In order to obtain the analytical expression for the poles of $\tilde{C}(z)$ for $\tau < \tau_c$ region, we first derive a general relation between real and imaginary parts of the poles. To this end we decompose f(z) into real and imaginary parts by substituting z=x+iy in Eq.(23). This provides

$$x(\tau) = -\frac{2}{\pi}g_1(x,y) \quad (A1)$$

$$y(\tau) = -\frac{2}{\pi}g_2(x,y) \quad (A2)$$

where

$$g_1(x,y) = \int_0^\infty sech(\hat{t})exp(-x\hat{t})cos(y\hat{t})d\hat{t} \quad (A3)$$

and

$$g_2(x,y) = -\int_0^\infty sech(\hat{t})exp(-x\hat{t})sin(y\hat{t})d\hat{t} \quad (A4)$$

(i) $\tau \leq \tau_c$

For $\tau \to \tau_c$ and hence for $x \to x_c$ it may be shown that the imaginary part y tends to zero. Therefore, the behaviour of the poles for $\tau \leq \tau_c$ can be investigated by expanding expressions (A3) and (A4) in powers of y up to terms of order y^3. Expanding Eq.(A1) we find that

$$x\tau + \frac{2}{\pi}\beta(\frac{x+1}{2}) - \frac{y^2}{\pi^4}\beta''(\frac{x+1}{2}) = 0 \quad (A5)$$

and

$$Y^2 = [4\pi(x\tau + \frac{2}{\pi}\beta'(\frac{x+1}{2}))/\beta''(\frac{x+1}{2})]. \quad (A6)$$

If we expand (A2) in terms of y we find

$$y^2 = 24\pi[\tau + \beta'(\frac{x+1}{2})]/\beta'''(\frac{x+1}{2}). \quad (A7)$$

Equating (A6) and (A7) in the limit $x \to x_c$ we obtain

$$x = \frac{\tau_c x)c}{\tau} + \frac{\tau - \tau_c}{\tau K'}, \quad (A8)$$

with

$$K' = \beta''(\frac{x_c+1}{2})/6\beta'(\frac{x_c+1}{2}). \quad (A9)$$

The imaginary part y however, can be obtained directly from equation (A7) in the limit $x \to x_c$. We get

$$y = [\frac{24\pi(\tau - \tau_c)}{\beta'''(\frac{x_c+1}{2})}]^{1/2} \quad (A9)$$

Eqs.(A8) and (A10) determine the real and imaginary parts of the poles for the region $\tau \leq \tau_c$.

(ii) $\tau \to 0$.

Putting x=0 in Eqs. (A1) and (A2) it may be shown that for $\tau = 0$ the poles are located on the imaginary axis at $y = \pm\infty$. The behaviour of poles in $\tau \to 0$ limit therefore, can be investigated from Eqs.(A1) and (A2) in the limits $x \to 0$ and $y \to \pm\infty$. In the zeroth order approximation we get

$$y(\tau) = -\frac{1}{\tau} \quad (A11)$$

and

$$x(\tau) = -\frac{1}{\tau}sech[\frac{\pi}{2\tau}] \quad (A12)$$

These equations determined the poles in $\tau \to 0$ limit.

References

[1] D.M.Heyes, Phys. Rev .B **37**, 5677 (1988).

[2] R. Vogelsang, C.Hohesel and G.Ciccotti, J. Chem. Phys. **86**, 6371 (1987).

[3] D.M.Heyes, J.Chem Soc. Faraday Trans 2 **79**, 1741 (1983); *ibid* **80**, 1363 (1984).

[4] D. Levesque and L.Verlet Mol.Phys. **61**, 143 (1987).

[5] A.J.C. Ladd, W.Edward Alley and B.J.Alder, J.Stat.Phys **48**, 1147 (1987)

[6] K.D.Hammonds and D.M.Heyes J.Chem Soc.Faraday Trans.2 **84** 705 (1988).

[7] J.P.Boon and S.Yip *Molecular Hydrodynamic* McGraw Hill: New York (1980).

[8] K.Tankeshwar, G.S Dubey and K.N.Pathak, J.Phys.C; **21** L811 (1988).

[9] K.Tankeshwar, K.N.Pathak and S.Ranganathan Phys.Chem.Liq. **22** 75 (1990).

[10] K.N.Pathak and K.Tankeshwar in *Correlation in Electronic and Atomic Fluids*, Ed. P.Jena, R.Kalia, P.Vashishta and M.P.Tosi; World Scientific (1990).

[11] K.Tankeshwar, K.N.Pathak and S.Ranganathan J.Phys.C: **20** 1618, (1989): *ibid* **1** 6193 (1989).

[12] D.M.Heyes and J.G.Powels, Mol.Phys. **71**, 781 (1990).

[13] Jan. A. Leegwater, J.Chem.Phys. **94** 7402 (1991).

[14] V.Denner and M.Wagner J.Chem.Phys. **81** 5034 (1984).

[15] I.S.Grodshteyn and I.M. Ryzhik *Table of Integrals Series and Product*, Academic Press (1965).

[16] R.Bansal and K.N.Pathak Phys.Rev.A **9** 2773 (1974), *ibid* **15** 2519 (1977).

FIGURE CAPTIONS

Fig.1 Fourier spectrum $G(\omega)$ of the auto-correlation function with sech(t) memory for different values of τ.

Fig.2 Graphical solution of Eq.(23) for real z = x. This determines the poles of $\tilde{C}(z)$ on the real axis.

Fig 3a Comparison between the numerically determined poles z_1 and z_2 and the approximate analytical expressions on the real z axis. Solid curve : numerical solution. solid circles : values of z_1 and z_2 determined from Eqs(28) and (29). Δ : obtained from Eqs(31) and (32). + : obtained from Eq.(33), :obtained from Eq.(36).

Fig.3b Comparison between the numerically determined imaginary part of poles ($Imz_1 = -Imz_2$). Solid curve : numerical results. + : from Eq(34) and solid circle : from Eq.(37).

Fig. 4 Numerically determined time correlation function C(t) in comparison with short time expansion (broken curve : Eq.(21)) and long time expansion (solid circles : Eq.(22)) for different values of τ.

Fig. 5 Comparison of time evolution of the auto correlation function among gaussian, secant hyperbolic and exponential memory approaches for parameter $\delta_2/\delta_1 = \pi$. Solid line : sech(t) memory, dashed dot: Gaussian memory and dashed line: exponential memory.

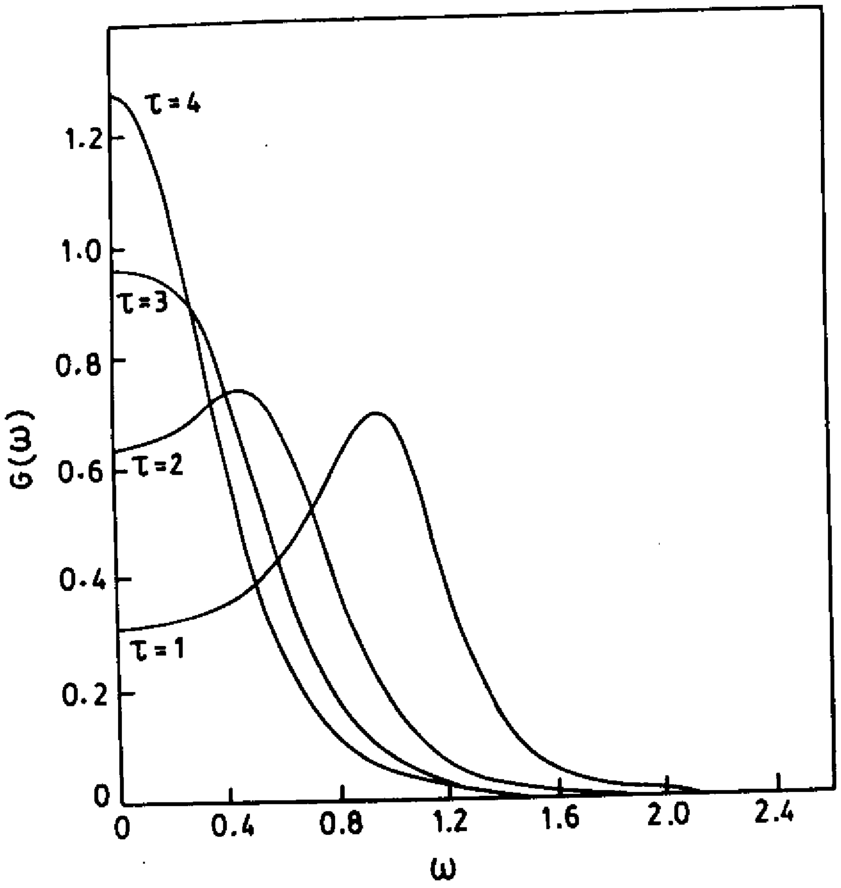
τ=4
τ=3
τ=2
τ=1
1.2
1.0
0.8
0.6
0.4
0.2
0
G(ω)
0
0.4
0.8
1.2
1.6
2.0
2.4
ω

Fig.1

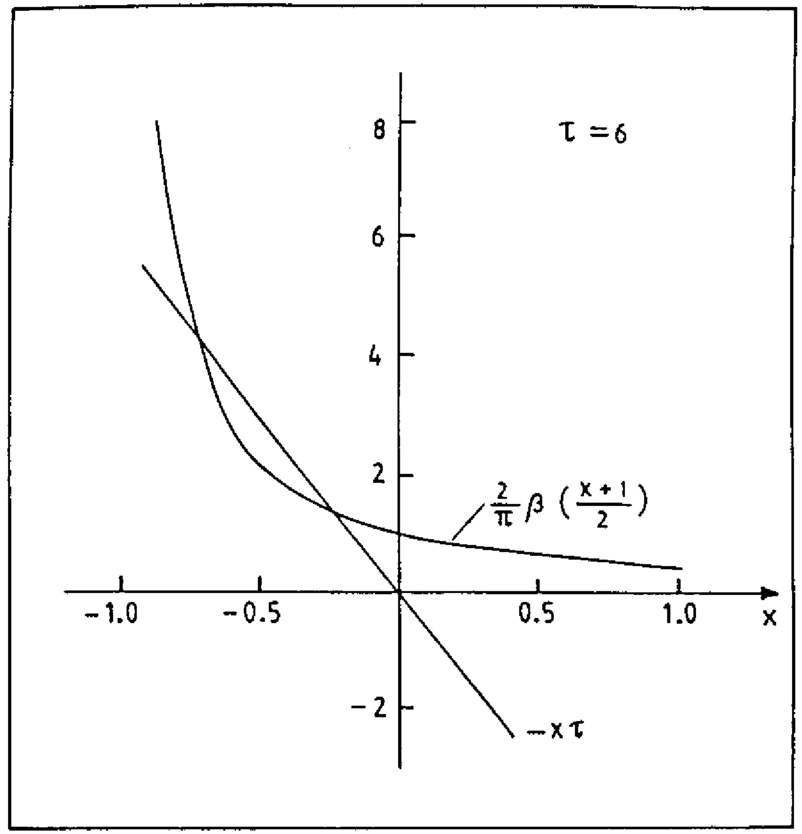
τ =6
8
6
4
2
−2
$\frac{2}{\pi}\beta\left(\frac{x+1}{2}\right)$
−1.0
−0.5
0.5
1.0
x
−xτ

Fig.2

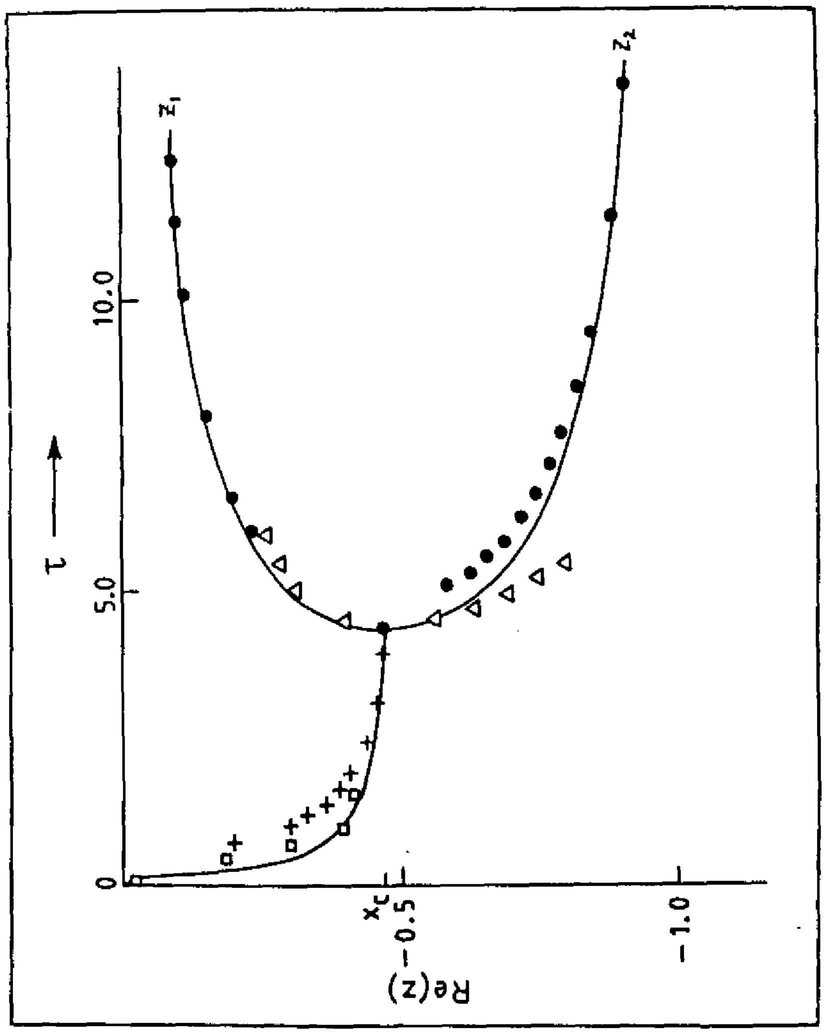

Fig.3a

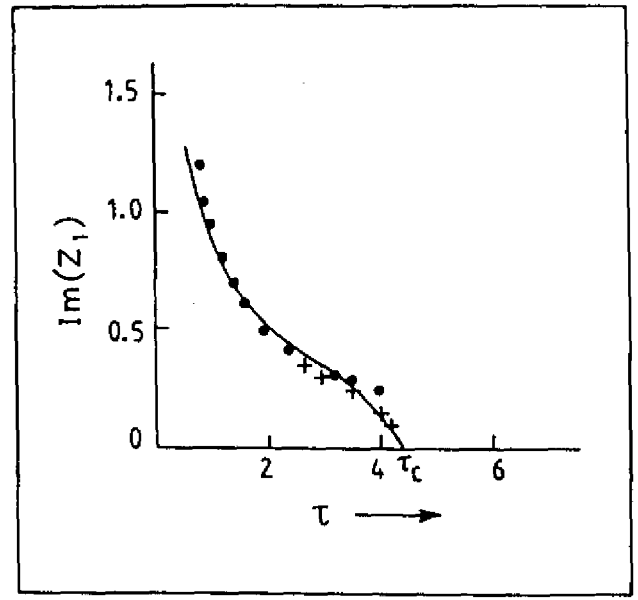

Fig.3b

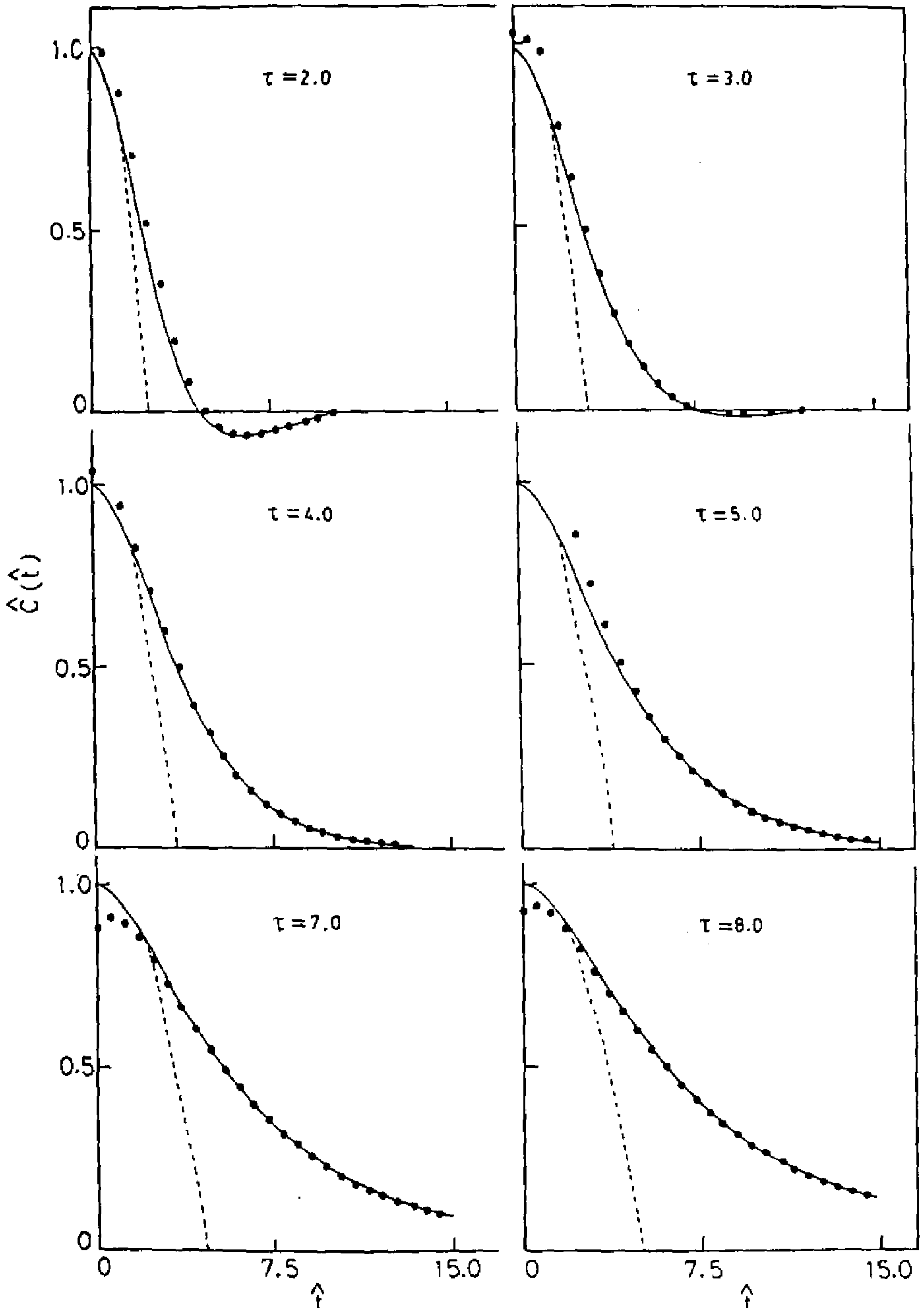
τ =2.0
τ =3.0
τ =4.0
τ =5.0
τ =7.0
τ =8.0
$\hat{c}(\hat{t})$
1.0
0.5
0
0
7.5
15.0
$\hat{t}$

Fig.4

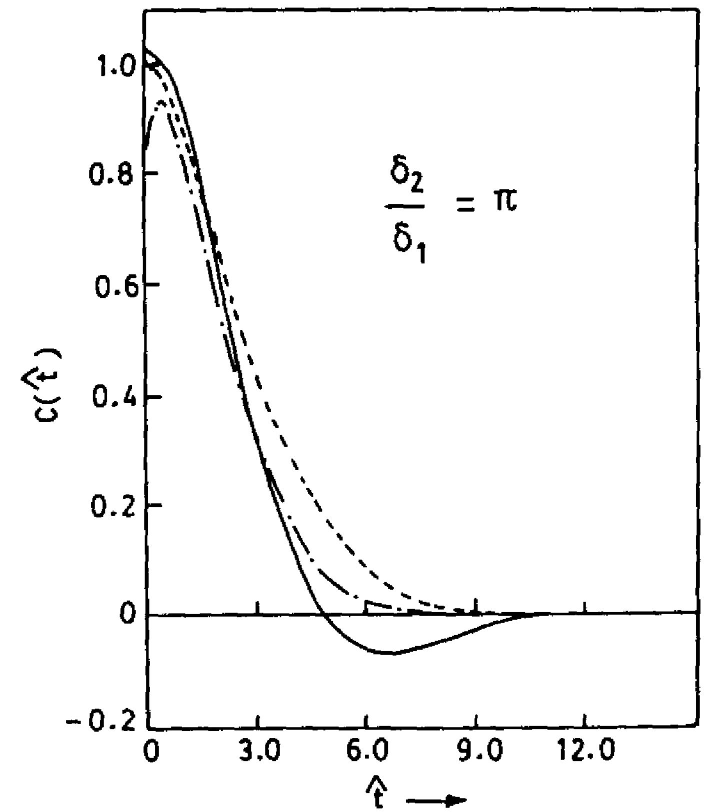
$\frac{\delta_2}{\delta_1} = \pi$
$c(\hat{t})$
1.0
0.8
0.6
0.4
0.2
0
-0.2
0
3.0
6.0
9.0
12.0
$\hat{t}$ →

Fig.5