Dynamics of gelling liquids: algebraic relaxation

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**Abstract**
The sol–gel system which is known, experimentally, to exhibit a power law decay of stress autocorrelation function has been studied theoretically. A second-order nonlinear differential equation obtained from Mori's integro-differential equation is derived which provides the algebraic decay of a time correlation function. Involved parameters in the expression obtained are related to exact properties of the corresponding correlation function. The algebraic model has been applied to Lennard-Jones and sol–gel systems. The model shows the behaviour of viscosity as has been observed in computer simulation and theoretical studies. The expression obtained for the viscosity predicts a logarithmic divergence at a critical value of the parameter in agreement with the prediction of other theories.

## 1. Introduction

One of the important aspects in the study of micro-dynamics of a physical system is the nature of relaxation processes. Depending on the nature of the physical system, the time correlation function, $\chi(t)$ of a given dynamical variable is known to relax differently. A few examples known in the wider class of systems for the study of dynamics are simple exponential, stretched exponential and algebraic decay. A time correlation function (TCF) for a dilute hard-sphere fluid [1] follows a simple exponential decay. On the other hand, in a system in which correlations become stronger, deviations from simple exponential [2] are observed. In complex systems the relaxation follows more complicated decays. For example, in the sol phase, i.e. well below the gelation transition, one observes a stretched exponential decay of the stress relaxation function. At the gelation transition, which sees the transformation of a viscous fluid into an elastic amorphous solid, the stress relaxation is algebraic in time: $\chi(t) \sim t^{-\Delta}$ [3–5], which results in the logarithmic divergence of viscosity. Even for simple liquids, the time correlation function shows $t^{-d/2}$ ($d$ is dimension) behaviour at long time, known as the long time tail [6, 7]. The algebraic relaxation or power law decay has been observed in systems like spin glasses [8, 9], chaotic systems [10], hierarchical Ising models [11], etc.

In the present work, Mori's memory function formalism has been used to understand the conditions under which a stress time correlation function transforms from a simple decaying function to a power law decay leading to logarithmic divergence of viscosity. One of the theoretical methods to study time development of the TCF of a fluid is by making use of the Mori–Zwanzig equation [12, 13]. This method reduces the problem of evaluating the time evolution of a TCF to the calculation of an appropriate memory function. Owing to the presence of a projection operator and the requirement of knowing the time dependence of the dynamical variable involved, the microscopic calculation of the memory function becomes a complicated task for real physical systems. However, the memory function involved is also known to follow Mori's equation, leading to a hierarchy of equations introducing higher-order memory functions. Various truncation schemes to break the hierarchy of these sets of equations have been suggested [14–18]. A few such schemes express a higher-order memory function in terms of a lower-order memory function. Following a similar procedure in the present work, we use Mori's equation to derive a new form of the time correlation function which decays algebraically, resulting in power law behaviour of the correlation function. We find that a second-order nonlinear differential equation with a hyperbolically decaying solution, at some critical value of the parameter, transforms to another differential equation whose solution is algebraic in time. Such a transformation is seen in the sol–gel transition. It is found that our model could provide reasonably good results for the sol–gel system in agreement with the existing theories.

The layout of this paper is as follows. In section 2, we present the necessary theoretical steps. In section 3, we present results and discussion. Section 4 contains the summary and conclusion.

## 2. Theory

Transport coefficients can be written as a time integral of an appropriate time correlation function with the help of the Green–Kubo relation given as

$$\kappa = K \int_0^\infty \chi(t)\,dt, \qquad (1)$$

where $\kappa$ represents a transport coefficient, $\chi(t)$ is an appropriate TCF and $K$ is some thermodynamic quantity. In particular, $\kappa$ would represent shear viscosity if $\chi(t)$ is the transverse stress autocorrelation function. Mori's equation of motion, which determines the time evolution of a time correlation function, $\chi(t)$, is given as

$$\frac{d\chi(t)}{dt} + \int_0^t M_1(t-\tau)\chi(\tau)\,d\tau = 0, \qquad (2)$$

where $M_1(t)$ is the first-order memory function which is known to satisfy an equation similar to equation (2), i.e.

$$\frac{dM_1(t)}{dt} + \int_0^t M_2(t-\tau)M_1(\tau)\,d\tau = 0. \qquad (3)$$

Combining equations (2) and (3) we get

$$\frac{d^2\chi(t)}{dt^2} + \delta_1\chi(t) + \int_0^t M_2(t-\tau)\frac{d\chi(\tau)}{d\tau}\,d\tau = 0, \qquad (4)$$

with $\delta_1 = M_1(0)$. Now we make use of an approximation to write the integrand as a product of two independent functions of $t$ and $\tau$:

$$M_2(t-\tau)\frac{d\chi(\tau)}{d\tau} \rightarrow M_2(t)\frac{df(\chi(\tau))}{d\tau}$$
$$= M_2(t)\frac{\chi^\alpha(\tau)}{\chi^\alpha(0)}\frac{d\chi(\tau)}{d\tau}. \qquad (5)$$

This approximation is exact for $\tau = 0$ and provides a correction to the Markovian approximation for $\tau < t$. Writing $M_2(t-\tau)$ as a product of two functions implies that, for a function even in time, the coupling between $t$ and $\tau$ is ignored. Alternatively, this approximation implies that the integral (area) to be estimated is replaced approximately by an equivalent area. The approximation (5) need not be seen in isolation. Using equations (4) and (5) we obtain the following differential equation:

$$\frac{d^2\chi(t)}{dt^2} + \delta_1\chi(t) + M_2(t)\frac{(\chi^{\alpha+1}(t) - \chi^{\alpha+1}(0))}{(\alpha+1)\chi^\alpha(0)} = 0. \qquad (6)$$

We further assume the following form for $M_2(t)$:

$$M_2(t) = A\frac{\chi^{\alpha+2}(t)}{\chi^{\alpha+2}(0)} + B\frac{\chi(t)}{\chi(0)}. \qquad (7)$$

This approximation is similar to the ideas used in super-cooled liquids and glass transition theory based on the feedback phenomenon [19]. From equations (6) and (7) we obtain

$$\frac{d^2\chi(t)}{dt^2} + \left(\delta_1 - \frac{B}{\alpha+1}\right)\chi(t) + \frac{(B-A)}{(\alpha+1)}\frac{\chi^{\alpha+2}(t)}{\chi^{\alpha+1}(0)}$$
$$+ \frac{A\chi^{2\alpha+3}(t)}{(\alpha+1)\chi^{2\alpha+3}(0)} = 0. \qquad (8)$$

One of the solutions of this equation is given by

$$\chi(t) = \frac{\chi(0)(1+\gamma)^{\frac{1}{\alpha+1}}}{(1+\gamma\,\cosh(kt))^{\frac{1}{\alpha+1}}}, \qquad (9)$$

for $\alpha$ not equal to $-1$. In the above expression

$$k = [(\alpha+1)(B-\delta_1(\alpha+1))]^{\frac{1}{2}},$$

$$\gamma = \frac{\delta_1}{B-\delta_1(\alpha+2)},$$

and

$$B = \frac{\delta_1(\alpha+2)(\alpha+3) - \delta_2}{(\alpha+1)}.$$

The $\delta_n$ are related to sum rules of the corresponding TCF through the following relations:

$$\delta_1 = \frac{\chi_2}{\chi_0} \qquad \text{and} \qquad \delta_2 = \frac{\chi_4}{\chi_2} - \frac{\chi_2}{\chi_0},$$

where $\chi_0$, $\chi_2$ and $\chi_4$ are zeroth, second and fourth sum rules of TCF and are given by the coefficient of short time expansion:

$$\chi(t) = \chi_0 - \frac{t^2}{2!}\chi_2 + \frac{t^2}{4!}\chi_4 - \cdots. \qquad (10)$$

All the parameters appearing above can be related to these sum rules, expressions for which can be obtained exactly.

For $\gamma = 1$, equation (9) reduces to the following expression:

$$\chi(t) = \chi_0\,\text{sech}^\nu\left(\sqrt{\frac{\chi_2}{\nu}}t\right), \qquad (11)$$

with $\nu = 2/(\alpha+1)$. Equations (9) and (11) both satisfy sum rules exactly up to fourth order. Equation (9) has an additional parameter $\alpha$ and this does not affect the short time properties of the TCF. These forms (equations (9) and (11)) of MF was derived earlier by us [15, 16] which decay without showing any sign of slow dynamics being observed at long times in highly viscous liquids or glasses.

On the other hand, if we take $B = (\alpha+1)\delta_1$, we obtain from equation (8) another nonlinear differential equation given as

$$\frac{d^2\chi(t)}{dt^2} - \frac{2b(\beta+2)}{\beta^2}\chi^{\beta+1}(t) + \frac{4ab(\beta+1)\chi^{2\beta+1}(t)}{\beta^2} = 0, \qquad (12)$$

where

$$\beta = \alpha+1, \qquad a = \chi_0^{-\beta}, \qquad b = 2\delta_1\frac{\beta(\beta+1)}{A}.$$

Here, it may be recalled that the parameter $B$ determines the strength of the coefficient of the linear term in equation (7). It is found that one of the solutions of equation (12) is

$$\chi(t) = \frac{1}{(a+bt^2)^{1/\beta}}, \qquad (13)$$

which makes $\chi(t)$ to decay algebraically with long time behaviour as $t^{-2/\beta}$. Thus, it is noted that by choosing different strengths of the parameter $B$, $\chi(t)$ transforms from
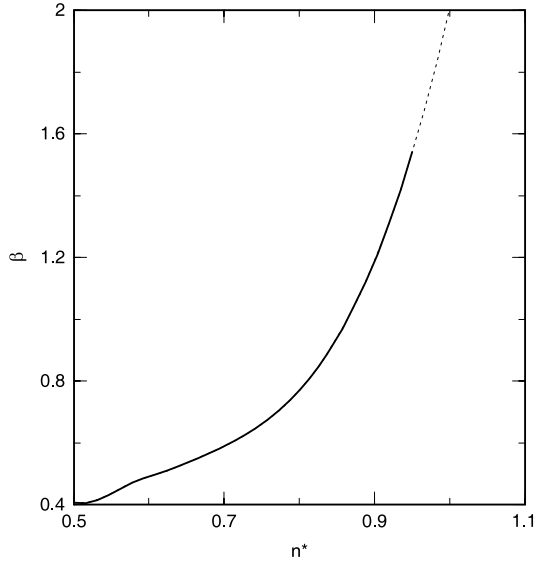
**Figure 1.** Variation of $\beta$ with $n^*$. The solid line is the result obtained using theoretical results of sum rules. The dotted line is an extrapolation up to 2.
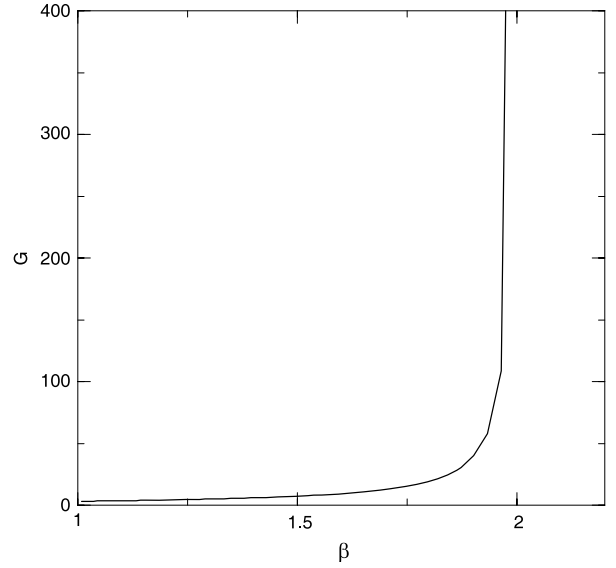


**Figure 2.** Variation of $G(\beta)$ with $\beta$. Divergence of $G(\beta)$ leads to divergence of viscosity.

exponential-like behaviour to algebraic behaviour with a long time tail. Here, it may be noted that $\chi(t)$ given by equation (13) provides short time properties of the time correlation function of the classical system and also shows power law behaviour at long time. So the algebraic function can cover the decay of the correlation function exhibited by a wide class of liquids ranging from inert fluids to gel liquids. Substituting equations (13) in (1), we obtain the following expression for the transport coefficient:

$$\kappa = K \int_0^\infty \frac{1}{(a + bt^2)^{1/\beta}} \, dt = \frac{K}{2a^{1/\beta}} \left( \frac{a}{b} \right)^{1/2} G(\beta), \quad (14)$$

where

$$G(\beta) = \frac{\Gamma(\frac{1}{2})\Gamma(\frac{1}{\beta} - \frac{1}{2})}{\Gamma(\frac{1}{\beta})}. \quad (15)$$

Comparing the exact short time expansion of $\chi(t)$ with that given by equation (13) we obtain

$$\frac{b}{a} = \frac{1}{6} \left( \frac{\chi_4}{\chi_2} - 3\frac{\chi_2}{\chi_0} \right), \quad (16)$$

and

$$\beta = \frac{(\chi_4 \chi_0 - 3\chi_2^2)}{3\chi_2^2}. \quad (17)$$

It can be seen that for $\beta = 2$, $\chi(t)$ decays as $t^{-1}$ and $\kappa$ diverges logarithmically. For $\beta = 2$ it is noted that $\chi_4 \chi_0 = 9\chi_2^2$. Expression (14) for shear viscosity $\eta$, with $K = \frac{1}{Vk_BT}$ and $\chi(t)$ as the stress correlation function, reduces to

$$\eta = \frac{n}{k_B T} \frac{\chi_0}{\sqrt{2\beta\delta_1}} G(\beta), \quad (18)$$

where $n$, $T$ and $k_B$ represent the number density, temperature of the system and Boltzmann's constant, respectively. We apply these formulations to study the viscosity of the system which undergoes the gelation transition.

## 3. Results and discussion

To examine the utility of the memory function derived above, we first study the behaviour of the parameter $\beta$. In order to calculate the parameter $\beta$ from equation (17), we require sum rules of the stress autocorrelation function up to fourth order. Expressions for the sum rules and their numerical results are available [20] for Lennard-Jones systems. Therefore, we calculate $\beta$ for various densities $n^* = n\sigma^3$ at $T^* = k_B T/\epsilon = 1.06$, where $\epsilon$ and $\sigma$ are well depth and position of the first zero of the LJ potential. The results obtained are shown as a full line in figure 1. The dotted line is an extension to $\beta = 2$; a point of divergence of viscosity represents an ideal transition point. From figure 1, it can be seen that $\beta$ becomes equal to 2 at a density $n^* \approx 1.00$. Viscosity rises to many orders of magnitude just below this transition point. In order to show this explicitly, we plot $G(\beta)$ appearing in equation (18) as a function of $\beta$ in figure 2. From figure 2 it can be seen that $G(\beta)$ rises by two orders of magnitude as one goes from $\beta = 1.2$ to 1.97. The value of $\beta$ at the triple point is found to be 1.44, which implies that $\chi(t)$ goes as $t^{-1.39}$, which is to be compared with $t^{-d/2}$ for $d = 3$. We have also found that $\beta$ decreases with the increase in temperature and with the decrease in density. At $T^* = 1.06$ and $n^* = 0.5$, the value of $\beta$ is 0.95 and $\chi(t)$ at long times goes as $t^{-2.1}$. The values of shear viscosity calculated from equation (18) at this density and other densities and temperatures are within 15% from the computer simulation results [21]. Thus, the model is able to provide very reasonable results for the viscosity and is also able to give an estimate about the density and temperature which may correspond to the glassy/amorphous phase.

A better system where we shall apply our model is a sol–gel system. In a sol–gel system where power law behaviour has been observed experimentally, the timescale relevance to such a system is of the order of microseconds. We first of all plot $\chi(t)$ versus $t$ (s) in figure 3 and compare it with
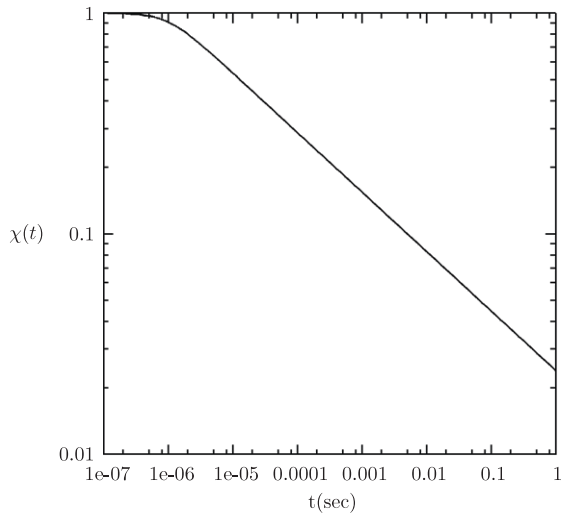
**Figure 3.** Variation of $\chi(t)$ with $t$ (s) plotted logarithmically. The power decay after a few microseconds becomes evident.



**Figure 4.** Plot of viscosity $\eta(c)$ versus $(c - 0.7464)$ for $L = 20$ for three dimensions. Solid line represents results obtained from equation (18) whereas squares represent results taken from the work of Broderix *et al* [5].

that observed by Martin and Wilcoxon [3]. In figure 3, we set $\beta = 0.135$, so as to assign $t^{-0.27}$ behaviour for long times, observed experimentally. It is found that our results, then, are quite similar to the experimental results [5] over the whole of the time domain. It was pointed out by Martin and Wilcoxon [3] that, at short times of the order of microseconds, the correlation function has decayed exponentially. This is taken care of by the coefficient of short time expansion. The expression derived here is made to satisfy short time properties through parameters $a$ and $b$. Here, it can also be seen that, after a few microseconds, the correlation in logarithmic scale decays linearly up to many decades, implying power law decay of the correlation function.

Next, we attempt to fit the values of viscosity in a sol–gel system obtained through the following relation [5]:

$$\eta(c, L) = L^{k/\nu} \bar{\eta}[(c - c_{\text{crit}})L^{1/\nu}], \qquad (19)$$

which is similar to finite size scaling relations for the percolation transition. Here $\bar{\eta}$ is a universal function and $\nu$ is the exponent describing the divergence of correlation length. The values of critical exponent $k$ and $\nu$ are 0.75 and 0.88, respectively. Results for $L = 10, 13, 16$ and 20 collapse onto one curve near the critical concentration. We transform linearly $\beta$ to $2 + (c - 0.7464)L^{1.14}$ in equation (19), keeping the rest of the parameters as constant. The results obtained are shown as a solid line in figure 4 for $L = 20$; the results given by Broderix *et al* [5] are also shown as solid circles. It can be seen that our expression obtained for viscosity can be used to fit the values of viscosity obtained from scaling relation (equation (19)).

## 4. Summary and conclusion

In this work, a nonlinear differential equation derived from Mori's equation using two plausible approximations has been transformed into another differential equation, which makes the time correlation function to decay in algebraic fashion. The algebraic relaxation of the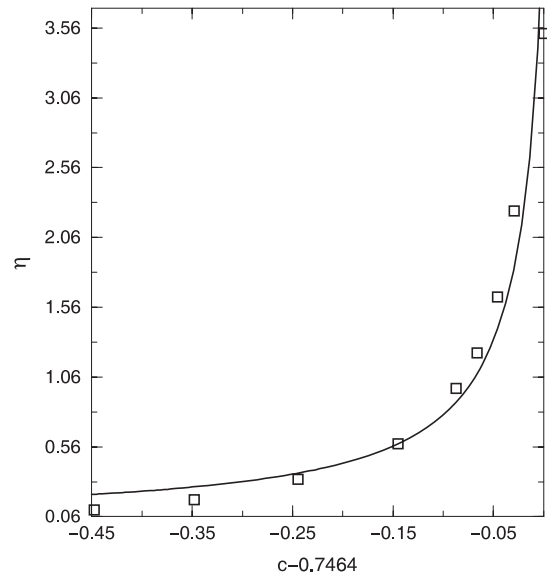 stress correlation function leads to logarithmic divergence of viscosity at particular values of the parameter. The algebraic relaxation model has been used to study viscosity in the Lennard-Jones system and sol–gel systems. It is found that the model could provide reasonably good results for sol–gel and Lennard-Jones systems in agreement with the existing theories.

## Acknowledgments

## References

[1] McQuaire D A 1976 *Statistical Mechanics* (New York: Harper and Row)
[2] Alder B J and Wainwright T E 1967 *Phys. Rev. Lett.* **18** 988
[3] Martin J E and Wilcoxon J P 1988 *Phys. Rev. Lett.* **61** 373
[4] Martin J E, Adolf D and Wilcoxon J P 1988 *Phys. Rev. Lett.* **61** 2620
[5] Broderix K, Aspelmeier T, Hartmann A and Zippelius A 2001 *Phys. Rev.* E **64** 021404
[6] Löwe H, Müller P and Zippelius A 2005 *J. Phys.: Condens. Matter* **17** S1659
[7] Bellisent-Funel M C, Loggeville S, Zanotti M and Chen S H 2000 *Phys. Rev. Lett.* **85** 3644
[8] Takahashi K and Takeda K 2008 *Phys. Rev.* B **78** 174415
[9] Keren A, Bazalitsky G, Campbell I and Lord J S 2001 *Phys. Rev.* B **64** 054403
[10] Armstead D, Hunt B R and Ott E 2002 *Phys. Rev. Lett.* **89** 284101
[11] Kutasov D, Aharony A, Domany E and Kinzel W 1986 *Phys. Rev. Lett.* **56** 2229
[12] Boon J P and Yip S 1980 *Molecular Hydrodynamics* (New York: McGraw-Hill)

[13] Hansen J P and MacDonald I R 1986 *Theory of Simple Liquids* (New York: McGraw-Hill)

[14] Tankeshwar K and Pathak K N 1995 *J. Phys.: Condens. Matter* **7** 5729

[15] Singh S, Kumar C N and Tankeshwar K 2002 *Mod. Phys. Lett.* B **16** 739

[16] Singh S, Srivastava S, Kumar C N and Tankeshwar K 2003 *Phys. Chem. Liq.* **41** 567

[17] Yulmteyev R M, Moskshin A V and Hanggi P 2003 *Phys. Rev.* E **68** 051201

[18] Balucani U, Lee M H and Tognetti V 2003 *Phys. Rep.* **373** 409

[19] Jacobs R L 1986 *J. Phys. C: Solid State Phys.* **19** L119

[20] Tankeshwar K, Pathak K N and Ranganathan S 1988 *J. Phys. C: Solid State Phys.* **21** 3607

[21] Heyes D M 1983 *J. Chem. Soc. Faraday Trans.* II **79** 1741
Heyes D M 1984 *J. Chem. Soc. Faraday Trans.* II **80** 1363