Time-dependent friction and solvation time correlation function

Alok Samanta\textsuperscript{1}, Sk Musharaf Ali\textsuperscript{2} and Swapan K Ghosh\textsuperscript{1,3}

\textsuperscript{1} Theoretical Chemistry Section, RC and CD Division, Chemistry Group, Bhabha Atomic Research Centre, Mumbai 400 085, India
\textsuperscript{2} Chemical Engineering Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
\textsuperscript{3} E-mail: skghosh@magnum.barc.ernet.in

New Journal of Physics 7 (2005) 27
Received 30 August 2004
Published 31 January 2005
Online at http://www.njp.org/
doi:10.1088/1367-2630/7/1/027

Abstract. We have derived a new relation between the time-dependent friction and solvation time correlation function (STCF) for non-polar fluids. The friction values calculated using this relation and simulation results on STCF for a Lennard–Jones fluid are shown to have excellent agreement with the same obtained through mode-coupling theory. Also derived is a relation between the time-dependent dielectric friction and STCF for polar fluids. Routes are thus provided to obtain the time-dependent friction (non-polar as well as dielectric) from an experimentally measured quantity like STCF, even if the interparticle interaction potential is not known.

Contents

1. Introduction 2
2. Theoretical formalism 3
3. Time-dependent friction from MCT 6
4. Results and discussion 8
5. Conclusion 10
Acknowledgments 10
Appendix. Time-dependent dielectric friction and STCF 10
References 12

\textsuperscript{3} Author to whom any correspondence should be addressed.
1. Introduction

Time-dependent friction has played a central role over the years in connection with studies on diffusion and activated barrier crossing processes [1] in the condensed phase. Despite an immense interest in friction, the precise role and quantification of this quantity for a fluid with unknown interparticle interaction potential still remain elusive. In various physical and chemical processes, one needs to know how the dynamical friction varies over a wide range of time and hence it is of interest to have a suitable prescription with proper validity over the entire time range. Generalized hydrodynamic theory can, however, describe only the long-time behaviour of the dynamical friction, whereas suitable modelling has provided an accurate short-time behaviour. For most of the physicochemical processes, however, neither of the above two limits hold, and hence a microscopic theory for a proper description of friction over a wide range of time is very much needed. Among the theoretical approaches, a recent and successful approach is the kinetic mode-coupling theory (MCT) [2, 3], which provides a self-consistent iterative scheme to evaluate the time-dependent friction as well as diffusivity for pure fluids and fluid mixtures [6]–[8] in terms of various static and dynamical quantities such as the equilibrium pair correlation function, collective dynamic structure factor and transverse current correlation. MCT, however, requires an explicit knowledge of the interparticle interaction potential and hence is used mainly for fluids with model interaction potential. For a fluid with an unknown interaction potential, it is thus a formidable task to obtain the dynamical friction, which is also not accessible through direct experimental measurement. Thus, it would be worthwhile to find an indirect experimental probe for the friction by relating it to some other suitable quantity measurable experimentally.

The time-dependent friction is mainly due to the frictional drag experienced by the solute particle in the presence of the solvent motion around it. Therefore, it is expected that the study of other phenomena which also involve solvent motion will provide information about friction. It is well known that the study of solvation dynamics is concerned with the dynamical response of the solvent when there is an electronic redistribution of the solute species upon optical excitation, which causes an abrupt change in the interaction of the solute with the surrounding solvent molecules, thus resulting in a new potential energy surface for the system. The subsequent equilibration process involving the solute and the solvent molecules on this new potential energy surface is investigated through solvation dynamics as reflected in the time dependence of fluorescence Stokes shift, measured in time-resolved fluorescence and transient hole burning experiments [9]–[12]. Thus, it is expected that there should be an intimate connection between the solvation time correlation function (STCF) and the time-dependent friction. Most of the theoretical treatments of solvation dynamics assume the validity of linear response, which allows one to directly relate the time-dependent Stokes shift to the equilibrium STCF. Therefore, if one is able to establish a relation between the time-dependent friction and STCF, it is possible to obtain the former directly from the experimental results for complex systems for which the interparticle potential is not known. A linear relation between the STCF and dielectric friction has previously been derived using continuum theory [13], the validity of which has, however, not been tested. Also, no relation between STCF and the time-dependent friction has been obtained for non-polar fluids. Moreover, continuum theory may not work in the intermediate- to high-density region where the molecular nature of the solvent plays an important role. Therefore, the objective of this work was to derive a relation between the STCF and time-dependent friction for non-polar as well as polar fluids by using the microscopic definition of STCF.
In what follows, we develop the theoretical formalism relating the time-dependent friction with STCF for non-polar fluids in section 2 and polar fluids in the appendix. This relation is tested through illustrative numerical results for Lennard–Jones (L-J) fluids in section 4 by evaluating the friction using this relation and comparing with the same calculated through MCT presented in section 3. Finally, we offer a few concluding remarks in section 5.

2. Theoretical formalism

We consider a solute particle immersed in a fluid containing \( N \) number of solvent particles with pairwise additive interparticle interaction. The equilibrium STCF \( S(t) \) is defined as

\[
S(t) = \int U_s(R, \{r\}) U_s(R^0, \{r^0\}) P(R, \{r\}, t|R^0, \{r^0\}, 0) P_{eq}(R^0, \{r^0\}) \, dR \, dR^0 \, dN \, dr^0,
\]

where \( U_s(R, \{r\}) \) represents the total solute–solvent interaction potential, which can be expressed in terms of the two-particle interaction potential \( u_s(|R - r|) \) as

\[
U_s(R, \{r\}) = \sum_{i=1}^{N} u_s(|R - r_i|)
\]

with \( R \) and \( \{r\} \) representing the solute coordinate and the set of solvent coordinates, respectively, at time \( t \), while \( R^0 \) and \( \{r^0\} \) represent the same at initial time. Throughout this work, for simplicity, we assume the potential to be isotropic, as applicable in the case of atomic fluids and spherical solutes. The quantity \( P(R, \{r\}, t|R^0, \{r^0\}, 0) \) represents the time-dependent probability distribution which satisfies the Smoluchowski equation

\[
\frac{\partial}{\partial t} P(R, \{r\}, t|R^0, \{r^0\}, 0) = \mathcal{L} P(R, \{r\}, t|R^0, \{r^0\}, 0)
\]

with the initial condition

\[
P(R, \{r\}, 0) = \delta(R - R^0) \prod_{i=1}^{N} \delta(r_i - r^0_i).
\]

Here, the Smoluchowski operator \( \mathcal{L} \) is defined as

\[
\mathcal{L} = \mathcal{L}^0 + \mathcal{L}',
\]

where

\[
\mathcal{L}^0 = D_s \nabla_R^2 + D_{sol} \sum_{i=1}^{N} \nabla r_i^2
\]

and

\[
\mathcal{L}' = \beta D_s \nabla_R \cdot [\nabla_R U_s(R, \{r\})] + \beta D_{sol} \sum_{i} \nabla r_i \cdot [\nabla r_i \cdot U_{sol}(\{r\})].
\]
with \( D_s \) and \( D_{sol} \) representing the solute and solvent diffusivity, respectively. Here, \( \beta (= 1/k_B T) \) represents the inverse temperature with \( k_B \) as the Boltzmann constant, and \( U_{sol}(r) \) denotes the total solvent–solvent interaction potential that can be expressed in terms of the two-particle interaction potential \( u_{sol}(|r_i - r_j|) \) as

\[
U_{sol}(r) = \sum_{j>i}^N u_{sol}(|r_i - r_j|). 
\]

In equation (1), \( P_{eq}(R, r) \) is the equilibrium distribution function given by

\[
P_{eq}(R, r) = \exp \{ -\beta [U_s(R, r) + U_{sol}(|r|)] \}. 
\]

The formal solution of equation (3) with the boundary condition defined in equation (4) can be obtained as

\[
P(R, t|R^0, r^0), 0 = P^{0}(R, r, t|R^0, r^0, 0) + \int_0^t dt' \int P^{0}(R, r, t - t'|R', r'), 0 \times \mathcal{L}' P^{0}(R', r', t'|R^0, r^0, 0) dR' dN' r' + \ldots , 
\]

where \( P^{0}(R, r, t|R^0, r^0, 0) \) represents the distribution function corresponding to the Smoluchowski equation (equation (3)) with \( \mathcal{L} = \mathcal{L}^0 \) and the same initial condition as in equation (4). Now, substituting equation (10) into (1), the expression for \( S(t) \) can be obtained as

\[
S(t) = \int U_s(R, r) U_s(R^0, r^0) P^{0}(R, r, t|R^0, r^0, 0) P_{eq}(R^0, r^0) dR dN r dR^0 dN^0 r^0 
\]

\[
+ \int U_s(R, r) U_s(R^0, r^0) \int_0^t dt' \int P^{0}(R, r, t - t'|R', r'), 0 \times \mathcal{L}' P^{0}(R', r', t'|R^0, r^0, 0) dR' dN' r' P_{eq}(R^0, r^0) dR dN r dR^0 dN^0 r^0 + \ldots . 
\]

It is clear from equation (10) that the first term on the right-hand side corresponds to the distribution of freely diffusing solute and solvent particles, whereas the successive terms contain the potential energy terms with increasing order. Similarly, in equation (11), the first term on the right is quadratic in potential energy terms, whereas the successive terms involve higher powers of these quantities. If the interparticle interaction is weak, the higher-order terms are expected to be small and can be neglected in comparison to the first term. Within this approximation, one can write

\[
S(t) = \int U_s(R, r) U_s(R^0, r^0) P^{0}(R, r, t|R^0, r^0, 0) P_{eq}(R^0, r^0) dR dN r dR^0 dN^0 r^0, 
\]

the time derivative of which can be written as

\[
\frac{d}{dt} S(t) = \int U_s(R, r) U_s(R^0, r^0) \mathcal{L} P^{0}(R, r, t|R^0, r^0, 0) \times P_{eq}(R^0, r^0) dR dN r dR^0 dN^0 r^0 = D_s S_s(t) + D_{sol} S_{sol}(t), 
\]

where \( S_s(t) \) and \( S_{sol}(t) \) are given by

\[
S_s(t) = \int U_s(R, r) U_s(R^0, r^0) \nabla R^2 P^{0}(R, r, t|R^0, r^0, 0) P_{eq}(R^0, r^0) dR dN r dR^0 dN^0 r^0 
\]

\[
S_{sol}(t) = \int U_s(R, r) U_s(R^0, r^0) \mathcal{L} P^{0}(R, r, t|R^0, r^0, 0) \times P_{eq}(R^0, r^0) dR dN r dR^0 dN^0 r^0. 
\]
The homogeneity of the system requires that

\[ a_s \]

using which equation (14) can be written as

\[ \text{reduces to} \]

\[ S_{sol}(t) = \int U_s(\mathbf{R}, \{\mathbf{r}\})U_s(\mathbf{R}^0, \{\mathbf{r}^0\}) \sum_i \nabla_{\mathbf{r}_i}^2 P^0(\mathbf{R}, \{\mathbf{r}\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, 0) \]

\[ \times P_{eq}(\mathbf{R}^0, \{\mathbf{r}^0\}) \, d\mathbf{R} \, d^N r \, d^N r^0. \]

(15)

The homogeneity of the system requires that \( P^0(\mathbf{R}, \{\mathbf{r}\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, 0) \) depends on the differences \( \mathbf{R} - \mathbf{R}^0 \) and \( \mathbf{r} - \mathbf{r}^0 \) and hence one can write

\[ \nabla_{\mathbf{R}}^2 P^0(\mathbf{R}, \{\mathbf{r}\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, 0) = -\nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{R}^0} P^0(\mathbf{R}, \{\mathbf{r}\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, 0), \]

(16)

using which equation (14) can be written as

\[ S_s(t) = -\int \nabla_{\mathbf{R}} U_s(\mathbf{R}, \{\mathbf{r}\}) \cdot \nabla_{\mathbf{R}^0} U_s(\mathbf{R}^0, \{\mathbf{r}^0\})P^0(\mathbf{R}, \{\mathbf{r}\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, 0) \]

\[ \times P_{eq}(\mathbf{R}^0, \{\mathbf{r}^0\}) \, d\mathbf{R} \, d^N r \, d^N r^0 - \beta \int \nabla_{\mathbf{R}} U(\mathbf{R}, \{\mathbf{r}\}) \cdot \nabla_{\mathbf{R}^0} U_s(\mathbf{R}^0, \{\mathbf{r}^0\}) \]

\[ \times U_s(\mathbf{R}^0, \{\mathbf{r}^0\})P^0(\mathbf{R}, \{\mathbf{r}\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, 0) P_{eq}(\mathbf{R}^0, \{\mathbf{r}^0\}) \, d\mathbf{R} \, d^N r \, d^N r^0 \]

\[ = -\langle F(t) F(0) \rangle - \beta (\nabla_{\mathbf{R}} U_s(\mathbf{R}, \{\mathbf{r}\}) \cdot \nabla_{\mathbf{R}^0} U_s(\mathbf{R}^0, \{\mathbf{r}^0\}) U_s(\mathbf{R}^0, \{\mathbf{r}^0\})), \]

(17)

where \( F(t) \) represents the total force acting on the solute particle. Here, the second term on the right represents the higher-order correlation contribution and can be neglected in comparison to the first term if the interaction energy is small. Within this approximation, equation (17) reduces to

\[ S_s(t) \simeq -\langle F(t) F(0) \rangle. \]

(18)

Similarly, using the same procedure and approximation, one can first express \( S_{sol}(t) \) of equation (15) as

\[ S_{sol}(t) \simeq -\sum_i \int \nabla_{\mathbf{r}_i} U_s(\mathbf{R}, \{\mathbf{r}\}) \cdot \nabla_{\mathbf{r}_i} U_s(\mathbf{R}^0, \{\mathbf{r}^0\})P^0(\mathbf{R}, \{\mathbf{r}\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, 0) \]

\[ \times P_{eq}(\mathbf{R}^0, \{\mathbf{r}^0\}) \, d\mathbf{R} \, d^N r \, d^N r^0, \]

(19)

which can be further approximated to obtain

\[ S_{sol}(t) \simeq -\langle F(t) F(0) \rangle. \]

(20)

It may be noted that since the expression given by equation (19) represents only the diagonal part of the force–force autocorrelation function \( \langle F(t) F(0) \rangle \), equation (20) involves an approximation of neglecting the off-diagonal contribution to this correlation function which is however expected to be small unless the density is very high. Combining now equations (13), (18) and (20), we obtain

\[ \frac{d}{dt} S(t) = -(D_s + D_{sol})(F(t) F(0)). \]

(21)

Now applying the Kirkwood relation for friction [14], given by

\[ \xi(t) = \frac{1}{3m_\text{s} k_B T} \langle F(t) F(0) \rangle, \]

(22)
one finally obtains a relation between the STCF $S(t)$ and the time-dependent friction $\xi(t)$ as

$$\frac{d}{dt} S(t) = -3m_s k_B T(D_s + D_{sol}) \xi(t),$$

(23)

where $m_s$ is the mass of the solute particle. The above equation also leads to the relation

$$\frac{\xi(t)}{\xi(0)} = \frac{S'(t)}{S'(0)},$$

(24)

which is an important result of this work. Here, $S'(t)$ denotes the time derivative of $S(t)$. This relation opens a new route to an indirect experimental determination of the time-dependent friction for a system with unknown interaction potential through the use of experimentally measured $S(t)$. While equation (24) has been derived for a non-polar solvent, an analogous expression can easily be obtained for ionic solutes in polar solvents involving dielectric friction and is given by

$$\frac{\xi(t)}{\xi(0)} = \frac{S'(t) + 2D_K S(t)}{S'(0) + 2D_K S(0)},$$

(25)

the derivation of which is presented in the appendix.

For the special case of $S(t)$ decaying exponentially, equations (24) and (25) simplify further and lead to the relation

$$\frac{\xi(t)}{\xi(0)} = \frac{S(t)}{S(0)},$$

(26)

which is the same as the one obtained earlier [13] for dielectric friction using the continuum theory. Therefore, any deviation from equation (26) shown by the two relations (equations (24) and (25)) implies non-exponential behaviour of $S(t)$.

Equations (24) and (25) thus provide a route to obtain $\xi(t)$ from the data on $S(t)$ obtained through some other means (e.g. experiments), for which explicit knowledge of the interaction potential is not needed. It will, however, be of interest to first test the validity of these equations for some systems with known interaction potential, by obtaining $S(t)$ and $\xi(t)$ through simulation or other theoretical methods. One of the commonly used theoretical approaches for calculating $\xi(t)$ is mode-coupling theory (MCT), which is discussed below.

3. Time-dependent friction from MCT

In MCT, several modes such as density, longitudinal current, transverse current, etc may contribute to the evaluation of $\xi(t)$. However, in the range of liquid density, the slowness of the structural relaxation makes density fluctuation the most important decay channel. Hence, in the liquid density range, one can approximate [2]–[5] $\xi(t)$ as

$$\xi(t) = \xi_B(t) + \xi_{dp}(t),$$

(27)

where $\xi_B(t)$ and $\xi_{dp}(t)$ represent the friction arising due to binary collision and density fluctuation, respectively. The binary friction $\xi_B$ can be assumed to be given by the Gaussian
approximation as [6]

\[
\xi_B(t) = \xi_B(0) \exp \left[ -\frac{\xi_B(0) t^2}{2m_s} \right],
\]

(28)

where \( \xi_B(0) \) is the initial value of the friction, given by the exact expression

\[
\xi_B(0) = \frac{\rho}{3m_s} \int d\mathbf{r} g_{12}(r) \nabla^2 u_s(r),
\]

(29)

where \( \rho \) is the bulk density of the fluid, \( g_{12}(r) \) is the radial distribution function and \( u_s(r) \) is the pair potential between the solute and solvent particles. The MCT expression [2, 6] for \( \xi_{\rho\rho}(t) \) is given by

\[
\xi_{\rho\rho}(t) = \frac{\rho k_B T}{8\pi^2 m_s} \int dq' (\hat{q} \cdot \hat{q}')^2 q'^2 \left[ c_{12}(q') \right]^2 \left[ F_s(q', t) - F^0_{\rho}(q', t) \right] F(q', t),
\]

(30)

where \( \hat{q} \) and \( \hat{q}' \) denote unit vectors along \( q \) and \( q' \), respectively. Here, \( c_{12}(q) \) is the direct correlation function between the solute and solvent particles and \( F_s(q, t) \), \( F^0_{\rho}(q, t) \), and \( F(q, t) \) represent the self-dynamic structure factor, inertial part of the self-dynamic structure factor and collective dynamic structure factor, respectively.

In the small wave vector limit [3], one can obtain an approximate expression of \( F_s(q, t) \) given by

\[
F_s(q, t) = \exp \left[ -D_s q^2 \left\{ t + \frac{m_s D_s}{k_B T} \left( \exp \left( -\frac{k_B T}{m_s D_s} t \right) - 1 \right) \right\} \right].
\]

(31)

where \( \psi(t) \) is the velocity autocorrelation function. Using the expression of \( \psi(t) \) in the Markovian limit, given by

\[
\psi(t) = \frac{k_B T}{m_s} \exp \left[ -\frac{k_B T}{m_s D_s} t \right],
\]

(32)

one obtains from equation (31) the following result:

\[
F_s(q, t) = \exp \left[ -D_s q^2 \left\{ t + \frac{m_s D_s}{k_B T} \left( \exp \left( -\frac{k_B T}{m_s D_s} t \right) - 1 \right) \right\} \right].
\]

(33)

The other quantity required for the evaluation of \( \xi_{\rho\rho}(t) \) using equation (30) is the collective dynamic structure factor \( F(q, t) \), which, in the well-known simple version of the viscoelastic model [3]–[5], is given by

\[
F(q, t) = s(q) \exp \left[ -\gamma(q) t \right],
\]

(35)

where \( s(q) \) is the static structure factor and \( \gamma(q) \) is defined as

\[
\gamma(q) = \frac{2\langle w_q^2 \rangle}{\left[ \pi \left( \langle w_L^2(q) \rangle - \langle w_q^2 \rangle \right) \right]^{1/2}}.
\]

(36)
Here, $\langle w_q^2 \rangle$ and $w_L^2(q)$ are given by

$$\langle w_q^2 \rangle = \frac{k_B T}{m_{sol}s(q)} q^2$$  \hspace{1cm} (37)

and

$$w_L^2(q) = 3 \frac{k_B T}{m_{sol}} q^2 + \frac{\rho}{m_{sol}} \int dr g(r) \frac{\partial^2 u_{sol}(r)}{\partial z^2} - \frac{\rho}{m_{sol}} \int dr g(r) \frac{\partial^2 u_{sol}(r)}{\partial z^2} \cos(qz),$$ \hspace{1cm} (38)

where $m_{sol}$ denotes the mass of a solvent particle.

4. Results and discussion

In order to test the theoretical formalism developed here, we employ MCT to calculate $\xi(t)$ whereas for $S(t)$ we make use of the available simulation results. The system that we choose is the L-J fluid with the solvent particles interacting through the familiar L-J potential

$$u_{sol}(r) = 4\epsilon_{sol} \left[ \left( \frac{\sigma_{sol}}{r} \right)^{12} - \left( \frac{\sigma_{sol}}{r} \right)^6 \right],$$ \hspace{1cm} (39)

where $\epsilon_{sol}$ is the well depth and $\sigma_{sol}$ the effective solvent diameter. The solute–solvent interaction potential $u_s(r)$ is also assumed to have the L-J form of equation (39) with the parameters $\epsilon_{sol}$ and $\sigma_{sol}$ replaced by $\epsilon_s$ and $\sigma_s$. The input quantities required for the MCT calculation of $\xi(t)$ here are $s(k), c_{12}^1(k)$ and $g(r)$, which are obtained here using the standard integral equation-based method with a bridge function adopted by Duh and Henderson [17].

We have calculated $\xi(t)/\xi(0)$ using the simulation results [15] of $S(t)$ in equations (24) and (26) and plotted these values in figure 1 for the neat L-J fluid (i.e. solute and solvent particles are indistinguishable) of reduced density $\rho^* (= \rho \sigma_{sol}^3) = 0.844$ and temperature $T^* (= k_BT/\epsilon_{sol}) = 0.728$. In order to obtain $S'(t)/S'(0)$ from $S(t)$, we have fitted the simulation data of $S(t)$ as $S(t) = \sum_{i=1}^3 P_i \exp[-Q_i t]$ with the parameters $P_i$ and $Q_i$ obtained through best fit. We have also calculated $\xi(t)$ using MCT and plotted the same also in figure 1. The diffusion constant $D_{sol}^* (= D_{sol} (\epsilon_{sol} \sigma_{sol}^2 / m_{sol})^{1/2})$ needed in this calculation has been taken as 0.034 as obtained from simulation [16]. It is clear from the figure that the predictions of $\xi(t)$ from equation (24) using simulation results for $S(t)$ are in excellent agreement with the calculated results based on MCT, thus demonstrating the accuracy of the derived relations (equations (23) and (24)). The simulation results of $S(t)$ used in the earlier relation (equation (26)), however, are found not to yield good results for the non-polar system considered here at intermediate time. In order to verify the derived relation (equation (23)) for a system where the solute and the solvent particles differ significantly, we also consider another system with the solute parameters $\epsilon_s/\epsilon_{sol} = (2.47)^{1/2}, \sigma_s/\sigma_{sol} = 1.11, m_s/m_{sol} = 6.51$ and $D_s$ calculated from $D_{sol}$ using the Stokes–Einstein relation $D_s = D_{sol} \sigma_{sol} / \sigma_s$. We have plotted in figure 2 $\xi(t)/\xi(0)$ calculated using MCT as well as the same predicted by equations (24) and (26) using simulation results for $S(t)$ for this system. Here also, the MCT results are found to be in very good agreement with the predictions of equation (24), thus justifying again the derived relation (equation (23)). Equation (26), which predicts a linear relation between STCF and the time-dependent friction, does not seem to hold good in this case. The deviation is, in fact, more prominent for this
Figure 1. Plot of $\xi(t)/\xi(0)$ versus time $t^* (= t/(m_{sol}\sigma_{sol}^2/\epsilon_{sol})^{1/2})$ for a tagged particle of a neat L-J fluid of density $\rho^* = 0.844$ and temperature $T^* = 0.728$. The solid line represents the MCT results calculated using equation (27). The line with closed circles represents results from the present approach using simulation data on $S(t)$ in equation (24), while the open circles represent the same corresponding to equation (26).

Figure 2. Plot of $\xi(t)/\xi(0)$ versus time $t^*$ for a tracer solute particle in a L-J fluid of density $\rho^* = 0.844$ and temperature $T^* = 0.728$. The parameters used for the solute particle are $\epsilon_s/\epsilon_{sol} = (2.47)^{1/2}$, $\sigma_s/\sigma_{sol} = 1.11$ and $m_s/m_{sol} = 6.51$. The symbols are the same as in figure 1.
asymmetric system. The numerical results thus demonstrate the applicability of the derived relation between the time-dependent friction and STCF. This provides an indirect experimental route to obtain the time-dependent friction through experimentally measured STCF.

5. Conclusion

Some of the new aspects of this work are highlighted as follows. This is the first time a new relation between the time-dependent friction and STCF for non-polar as well as polar fluids has been derived using a microscopic approach. The MCT-based calculated results of the time-dependent friction are shown to be in excellent agreement with the predictions of the derived relation using simulation results on STCF for L-J systems. The new derived relation thus provides a route to obtain the time-dependent friction (non-polar as well as dielectric) from an experimentally measurable quantity like STCF for fluids where the interaction potential is not known. It will be interesting to extend this formalism further to establish a relation between the rotational dielectric friction and the solvation time. Work in this direction is in progress.

Acknowledgments

It is a pleasure to thank Dr T Mukherjee and Shri Sandip K Ghosh for their encouragement.

Appendix. Time-dependent dielectric friction and STCF

The equilibrium STCF for an ion in a dipolar solvent can be written as an extension of equation (1) in the form

$$S(t) = \int U_{id}(\mathbf{R}, \{\mathbf{r}\}, \{\omega\}) U_{id}(\mathbf{R}^0, \{\mathbf{r}^0\}, \{\omega^0\}) P(\mathbf{R}, \{\mathbf{r}\}, \{\omega\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, \{\omega^0\}, 0) \times P_{eq}(\mathbf{R}^0, \{\mathbf{r}^0\}, \{\omega^0\}) d\mathbf{R} d^N\mathbf{r} d^N\omega d^N\mathbf{R}^0 d^N\mathbf{r}^0 d^N\omega^0,$$

(A.1)

where $U_{id}(\mathbf{R}, \{\mathbf{r}\}, \{\omega\}) = \sum_{k=1}^{N} u_{id}(|\mathbf{R} - \mathbf{r}_k|, \omega_k)$ represents the total solute–solvent interaction potential, with $\{\omega\}$ and $\{\omega^0\}$ denoting the set of angular coordinates for the solvent dipoles at time $t$ and 0, respectively. Here, $P(\mathbf{R}, \{\mathbf{r}\}, \{\omega\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, \{\omega^0\}, 0)$ represents the probability distribution obeying the Smoluchowski equation

$$\frac{\partial}{\partial t} P(\mathbf{R}, \{\mathbf{r}\}, \{\omega\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, \{\omega^0\}, 0) = \mathcal{L} P(\mathbf{R}, \{\mathbf{r}\}, \{\omega\}, t|\mathbf{R}^0, \{\mathbf{r}^0\}, \{\omega^0\}, 0),$$

(A.2)

with the initial condition $P(\mathbf{R}, \{\mathbf{r}\}, \{\omega\}, 0) = \delta(\mathbf{R} - \mathbf{R}^0) \prod_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r}_i^0) \prod_{i=1}^{N} \delta(\omega_i - \omega_i^0)$ and the Smoluchowski operator $\mathcal{L}$, defined as $\mathcal{L} = \mathcal{L}_{id}^0 + \mathcal{L}_{id}'$, where

$$\mathcal{L}_{id}^0 = D_s \nabla^2 \mathbf{R} + D_{sol} \sum_{i=1}^{N} \nabla^2 \mathbf{r}_i + D_R \sum_{i=1}^{N} \nabla^2 \omega_i$$

(A.3)
and

$$L_{id}' = \beta D_s \nabla_R \cdot \left[ \nabla_R U_{id}(R, \{r\}, \{\omega\}) + \beta D_{sol} \sum_{i}^{N} \nabla_{r_i} \cdot [\nabla_{r_i} \cdot U_{dd}(\{r\}, \{\omega\})] + \beta D_R \sum_{i}^{N} \nabla_{\omega_i} \cdot [\nabla_{\omega_i} \cdot U_{dd}(\{r\}, \{\omega\})], \right]$$

(A.4)

with $D_s$ and $D_{sol}$ representing the solute and solvent translational diffusivity and $D_R$ denoting the rotational diffusivity. Now, proceeding in a manner similar to that for the non-polar solvent as discussed earlier, one obtains

$$\frac{d}{dr} S(t) = \int U_{id}(R, \{r\}, \{\omega\})U_{id}(R^0, \{r^0\}, \{\omega^0\})L_{id}^0 P^0(R, \{r\}, \{\omega\}, t|R^0, \{r^0\}, \{\omega^0\}, 0)
\times P_{eq}(R^0, \{r^0\}, \{\omega^0\}) dR d^N r d^N \omega dR^0 d^N r^0 d^N \omega^0
= D_s S_s(t) + D_{sol} S_{sol}(t) + D_R S_R(t), \quad (A.5)$$

which is the analogue of equation (13). Here, $P^0(R, \{r\}, \{\omega\}, t|R^0, \{r^0\}, \{\omega^0\}, 0)$ denotes the probability distribution for free diffusion corresponding to $L = L_{id}^0$ in equation (A.2) and $S_s(t)$, $S_{sol}(t)$, and $S_R(t)$ are given by

$$S_s(t) = \int U_{id}(R, \{r\}, \{\omega\})U_{id}(R^0, \{r^0\}, \{\omega^0\})\nabla^2 L_{id}^0 P^0(R, \{r\}, \{\omega\}, t|R^0, \{r^0\}, \{\omega^0\}, 0)
\times P_{eq}(R^0, \{r^0\}, \{\omega^0\}) dR d^N r d^N \omega dR^0 d^N r^0 d^N \omega^0, \quad (A.6)$$

$$S_{sol}(t) = \int U_{id}(R, \{r\}, \{\omega\})U_{id}(R^0, \{r^0\}, \{\omega^0\})\sum_{i}^{N} \nabla_{r_i}^2 P^0(R, \{r\}, \{\omega\}, t|R^0, \{r^0\}, \{\omega^0\}, 0)
\times P_{eq}(R^0, \{r^0\}, \{\omega^0\}) dR d^N r d^N \omega dR^0 d^N r^0 d^N \omega^0, \quad (A.7)$$

and

$$S_R(t) = \int U_{id}(R, \{r\}, \{\omega\})U_{id}(R^0, \{r^0\}, \{\omega^0\})\sum_{i}^{N} \nabla_{\omega_i}^2 P^0(R, \{r\}, \{\omega\}, t|R^0, \{r^0\}, \{\omega^0\}, 0)
\times P_{eq}(R^0, \{r^0\}, \{\omega^0\}) dR d^N r d^N \omega dR^0 d^N r^0 d^N \omega^0. \quad (A.8)$$

Using the requirement of homogeneity of the system and earlier approximations, one can easily obtain the simplified expressions for $S_s(t)$ and $S_{sol}(t)$ as

$$S_s(t) \approx -\langle F(t)F(0) \rangle \quad (A.9)$$

and

$$S_{sol}(t) \approx -\langle F(t)F(0) \rangle. \quad (A.10)$$

Now, using the spherical harmonics expansion

$$P^0(R, \{r\}, \omega_1, \omega_2, \ldots, \omega_k, \ldots, \omega_N, t|R^0, \{r^0\}, \{\omega^0\}, 0)
= \sum_{l,m} a_{l,m}(R, \{r\}, \omega_1, \ldots, \omega_{k-1}, \omega_{k+1}, \ldots, \omega_N, t|R^0, \{r^0\}, \{\omega^0\}, 0)Y_{l,m}(\omega_k), \quad (A.11)$$

New Journal of Physics 7 (2005) 27 (http://www.njp.org/)
and the relation
\[ \nabla^2 \omega k Y_{l,m}(\omega k) = -l(l + 1)Y_{l,m}(\omega k), \] (A.12)
it is clear that only the \( Y_{1,0} \) term would contribute to the integral in equation (A.8) since the ion–dipole interaction potential \( u_{id}(|R - r_k|, \omega k) \) can be expressed in the form
\[ u_{id}(|R - r_k|, \omega k) = q \frac{(R - r_k)}{|R - r_k|^3} \cdot \vec{\mu}(\omega k), \] (A.13)
which contains \( Y_{1,0}(\omega k) \) only. Here, \( \vec{\mu} \) and \( q \) are the dipole moment of the solvent and the charge of the ion, respectively. This simplifies equation (A.8), which can now be written as
\[ S_R(t) = -2S(t). \] (A.14)
Combining equations (A.5), (A.9), (A.10) and (A.14), we obtain
\[ \frac{d}{dt} S(t) = -(D_s + D_{sol})\langle F(t)F(0) \rangle - 2D_R S(t). \] (A.15)
Now applying the Kirkwood relation for friction given by equation (22), one finally obtains a relation between the STCF \( S(t) \) and the friction \( \xi(t) \) as follows:
\[ \frac{d}{dt} S(t) = -3m_s k_B T(D_s + D_{sol})\xi(t) - 2D_R S(t), \] (A.16)
which, on rearrangement, leads to the equation
\[ \frac{\xi(t)}{\xi(0)} = \frac{S'(t) + 2D_R S(t)}{S'(0) + 2D_R S(0)}, \] (A.17)
which is the same as equation (25) and is an important result.

References

[1] Hanggi P, Talkner P and Borkovec M 1990 Rev. Mod. Phys. 62 251
[2] Sjogren L and Sjolander A 1979 J. Phys. C: Solid State Phys. 12 4369
[3] Balucani U and Zoppi M 1994 Dynamics of the Liquid State (Oxford: Clarendon)
[4] Balucani U, Vellauri R, Gaskell T and Duffy S F 1990 J. Phys.: Condens. Matter 2 5015
[5] Balucani U, Vellauri R and Gaskell T 1990 Nuovo Cimento D 12 511
[6] Ali Sk M, Samanta A and Ghosh S K 2001 J. Chem. Phys. 114 10419
[7] Samanta A, Ali Sk M and Ghosh S K 2001 Phys. Rev. Lett. 87 245901
[8] Samanta A, Ali Sk M and Ghosh S K 2004 Phys. Rev. Lett. 92 145901
[9] Maroccelli M, MacInnis J and Flemming G R 1989 Science 243 1674
[10] Hynes J T 1994 Charge transfer reactions and solvation dynamics Ultrafast Dynamics of Chemical Systems ed J D Simon (Boston: Kluwer)
[11] Yu J, Kang T J and Berg M 1991 J. Chem. Phys. 94 5787
[12] Larsen D S, Ohba K and Flemming G R 1999 J. Chem. Phys. 111 8970
[13] van der Zwan G and Hynes J T 1985 J. Phys. Chem. 89 4181
[14] Kirkwood J G 1946 J. Chem. Phys. 14 180
[15] Egorov S A, Denny R A and Reichman D R 2002 J. Chem. Phys. 116 5080
[16] Heyes D M 1988 Phys. Rev. B 37 5677
[17] Duh D M and Henderson D 1996 J. Chem. Phys. 104 6742

New Journal of Physics 7 (2005) 27 (http://www.njp.org/)