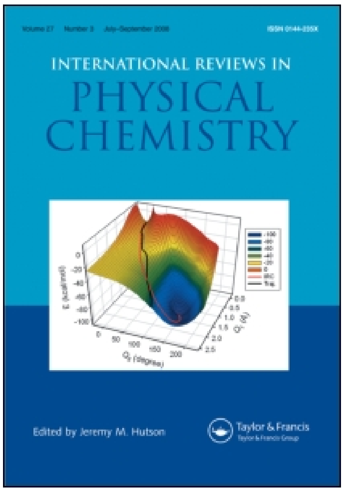


**International Reviews in Physical Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

# Orientational relaxation in dipolar systems: How much do we understand the role of correlations?

S. Ravichandran[a]; B. Bagchi[ab]
[a] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India [b] Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India

**To cite this Article** Ravichandran, S. and Bagchi, B.(1995) 'Orientational relaxation in dipolar systems: How much do we understand the role of correlations?', International Reviews in Physical Chemistry, 14: 2, 271 — 314

**To link to this Article: DOI:** 10.1080/01442359509353311

**URL:** http://dx.doi.org/10.1080/01442359509353311

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1995, VOL. 14, NO. 2, 271–314

# Orientational relaxation in dipolar systems: How much do we understand the role of correlations?

by S. RAVICHANDRAN and B. BAGCHI†
Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore-560012, India
† also at the Jawaharlal Nehru Centre for Advanced Scientific Research,
Bangalore, India

Dipolar systems, both liquids and solids, constitute a class of naturally abundant systems that are important in all branches of natural science. The study of orientational relaxation provides a powerful method to understand the microscopic properties of these systems and, fortunately, there are many experimental tools to study orientational relaxation in the condensed phases. However, even after many years of intense research, our understanding of orientational relaxation in dipolar systems has remained largely imperfect. A major hurdle towards achieving a comprehensive understanding is the long range and complex nature of dipolar interactions which also made reliable theoretical study extremely difficult. These difficulties have led to the development of continuum model based theories, which although they provide simple, elegant expressions for quantities of interest, are mostly unsatisfactory as they totally neglect the molecularity of inter-molecular interactions. The situation has improved in recent years because of renewed studies, led by computer simulations. In this review, we shall address some of the recent advances, with emphasis on the work done in our laboratory at Bangalore. The reasons for the failure of the continuum model, as revealed by the recent Brownian dynamics simulations of the dipolar lattice, are discussed. The main reason is that the continuum model predicts too fast a decay of the torque–torque correlation function. On the other hand, a perturbative calculation, based on Zwanzig's projection operator technique, provides a fairly satisfactory description of the single particle orientational dynamics for not too strongly polar dipolar systems. A recently developed molecular hydrodynamic theory that properly includes the effects of intermolecular orientational pair correlations provides an even better description of the single-particle orientational dynamics. We also discuss the rank dependence of the dielectric friction. The other topics reviewed here includes dielectric relaxation and solvation dynamics, as they are intimately connected with orientational relaxation. Recent molecular dynamics simulations of the dipolar lattice are also discussed. The main theme of the present review is to understand the effects of intermolecular interactions on orientational relaxation. The presence of strong orientational pair correlation leads to a strong coupling between the single particle and the collective dynamics. This coupling can lead to rich dynamical properties, some of which are detailed here, while a major part remains yet unexplored.

## 1. Introduction

Orientational relaxation of dipolar molecules in the condensed phases has been a subject of great interest for many decades. The most well-known work in this field is certainly the theory of Debye (1929), who used the rotational diffusion model to explain dielectric relaxation of dipolar liquids. Subsequently, a great number of experimental, theoretical, and most recently, computer simulation studies have been devoted to study orientational relaxation in a large number of dipolar liquids. The reason for sustained

0144–235X/95 $10·00

interest in the orientational relaxation of dipolar molecules is manyfold. First, the most important solvents for chemical industry consist of dipolar molecules, for example, water, acetonitrile, acetone, alcohols, to name a few. These liquids are also of great importance biologically. Naturally, there has always been a great interest in understanding the role of these solvents in chemical reactions, so much so that the field of orientational relaxation in dipolar liquids can now be regarded as a sub-field of chemical dynamics. Second, many spectroscopic experiments measure the orientational relaxation (Berne and Pecora 1976, Rothschild 1984). Not only dielectric relaxation, but also many other techniques, such as anisotropic Raman scattering and Kerr relaxation, probe orientational motion. Light scattering techniques are also sensitive to orientational relaxation. Although our understanding has increased continuously, several fundamental, problems have remained unsolved, as discussed below.

The theory of Debye (1929) provides a simple description of orientational relaxation. If we define the single particle orientational correlation functions $C_l(t)$ by the following expression

$$C_l(t) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \langle Y^*_{lm}[\Omega(0)Y_{lm}(\Omega(t))] \rangle, \tag{1}$$

where $Y_{lm}[\Omega(t)]$ are the usual spherical harmonics of angle, $\Omega(t)$, that describes the orientation of the tagged molecule at time $t$, then Debye's theory predicts that $C_l(t)$ decays exponentially in the following fashion

$$C_l(t) = \exp[-l(l+1)D_R t], \tag{2}$$

where $D_R$ is the rotational diffusion coefficient of the tagged molecule. If one makes the additional assumption that molecular rotations are independent of each other, then one arrives at the following simple expression of the frequency dependent dielectric function, $\epsilon(\omega)$

$$\epsilon(\omega) - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega\tau_D}, \tag{3}$$

where $\epsilon_0$ and $\epsilon_\infty$ are the zero and the infinite frequency dielectric constants of the liquid and $\tau_D = (2D_R)^{-1}$, is well-known Debye relaxation time. Equations (2) and (3) have been widely used to analyse experimental results and it is often assumed that they are equivalent which, however, is not correct—a fact first clearly addressed by Madden and Kivelson (1984). We shall discuss this point later.

The rotational diffusion model of Debye has been found to be fairly successful to explain orientational dynamics of non-polar molecules in simple non-polar liquids (Berne and Pecora 1976, Rothschild 1984, Fleming 1986, Ben-Amotz and Scott 1987). The situation is, however, considerably more complex for dipolar molecules. This is primarily because the dipolar interactions are long ranged. The interaction energy between two dipolar molecules separated by a vector distance $\mathbf{r}$ is given by

$$u_{ij}(\mathbf{r}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) = -\frac{3(\mathbf{r}\cdot\boldsymbol{\mu}_i)(\mathbf{r}\cdot\boldsymbol{\mu}_j)}{r^5} + \frac{\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j}{r^3}, \tag{4}$$

where $\boldsymbol{\mu}_i$ is the dipole moment of the $i$th molecule and $\mathbf{r}$ is the position vector between $i$th and $j$th molecules. The complex nature of this interaction potential has made fruitful analytical work prohibitively difficult. In view of these difficulties, a macroscopic description was developed quite early by using the continuum model based concepts—the aim was to include the effects of the long-range interaction in an average fashion. This approach was pioneered by Onsager (1936) who showed how to include correctly the reaction field effects, which arises from the electric polarization of the solvent by the rotating dipole, within the continuum model description. Onsager's expression for the static dielectric constant in terms of molecular properties has been extensively used by experimentalists (Fröhlich 1958, Böttcher and Bordewijk 1979) over the last half-century and, given its simple form, has been remarkably successful (Cole 1989). Subsequent theoretical studies, starting with Kirkwood (1936), have extended Onsager's theory in may directions and at present we seem to have a satisfactory theory for static properties of a simple dipolar liquid (Gray and Gubbins 1984, Wei and Patey 1990).

The situation, however, turned out to be considerably different for dynamics. Onsager's continuum model was extended to treat dielectric relaxation by Fatuzzo and Mason (1967) and by Nee and Zwanzig (1970). These theories employed a quasi-static boundary value calculation to obtain the time-dependent reaction field. Because of long-ranged dipolar interactions, the reaction field contains memory of past orientations and this makes the relaxation non-Markovian. This leads to a non-Debye behaviour of the dielectric relaxation, especially at larger frequencies. Nee and Zwanzig (1970) also presented a non-Markovian diffusion equation for the relaxation of the orientational correlation function, $C_l(t)$, and this equation is given by

$$\frac{\partial C_l(t)}{\partial t} = -l(l+1)\int_0^t \mathrm{d}\tau\, D_R(t-\tau)C_l(\tau), \tag{5}$$

where $D_R(t)$ is the time-dependent rotational diffusion coefficient. It is convenient to express the dynamical quantities as functions of the Laplace frequency, $z$; the Laplace transformed variable of any dynamical quantity $A(t)$ will be denoted by $\hat{A}(z)$. Equation (5) can then be written as

$$\hat{C}_l(z) = \frac{1}{z + l(l+1)\hat{D}_R(z)}. \tag{6}$$

The rotation diffusion coefficient $\hat{D}_R(z)$ was assumed to depend on the rotational friction through the Debye–Einstein relation

$$\hat{D}_R(z) = \frac{k_B T}{\hat{\zeta}_R(z)}, \tag{7}$$

where $k_B T$ is the Boltzmann constant times the temperature and $\hat{\zeta}_R(z)$ is the frequency-dependent rotational friction. In the continuum model studies it was further assumed that the frequency-dependent friction can be further decomposed into two parts that have different origins. That is,

$$\hat{\zeta}_R(z) = \zeta_0 + \hat{\zeta}_{DF}(z), \tag{8}$$

where $\zeta_0$ is the rotational viscous friction (due to Stokes law) that originates, primarily, from short-range angular interactions whereas $\hat{\zeta}_{DF}(z)$ is the friction entirely due to intermolecular dipolar interactions. Such as separation is usually justified by appealing to the long-range nature of dipolar interactions. The continuum model provides the following simple representation of $\hat{\zeta}_{DF}(z)$ in terms of $\epsilon(z)$.

$$\hat{\zeta}_{DF}(z) = \frac{2k_B T(\epsilon_0 - 1)[\epsilon(z) - \epsilon_0]}{z\epsilon_0[2\epsilon(z) + 1]}. \tag{9}$$

Since $\epsilon(z)$ itself depends on $\hat{\zeta}_{DF}(z)$, the connection formulae need to be solved self-consistently.

The continuum model based formulation of Nee and Zwanzig (1970) made several specific assumptions and approximations which need to be tested. It assumed a separation of time-scales between the decay of the single particle orientation and the torque–torque correlation function—the latter was assumed to decay much faster. It also neglected the rank ($l$) dependence of the dielectric friction. In an elegant application of the continuum mode, Hubbard and Wolynes (1978) removed the above and several other approximations. But the resulting theory, is still based on the continuum model description.

The major limitation of the continuum model is, however, not the simplifying assumptions made in deriving the required analytic expressions. Rather, it is the assumption that the interaction between any two molecules in the liquid can be approximated by the continuum electrostatic prescription. This assumption leads to the total neglect of pair correlations. Since these correlations are expected to be important when two molecules are close to each other (the separation distance is comparable to the molecular diameter), the continuum model can lead to a totally erroneous picture when we consider properties that are sensitive to small distances. An example is the force that is acting on a tagged dipolar molecule. Here the continuum model leads to an erroneous estimate of the force–force autocorrelation function.

The first systematic approach towards the formulation of a molecular theory of dielectric relaxation was taken by Madden and Kivelson (1982, 1984). These authors have contributed to many different aspects in this area and a few are summarized in the following. Among the most important things, a molecular theory of dielectric friction was developed (Madden and Kivelson 1984), in which they give the expression for dielectric friction which showed a strong rank ($l$) dependence. Madden and Kivelson's (1984) simple expression for the rank dependent dielectric friction can be written as

$$\zeta^{MK}_{DF,l} = \frac{2(\epsilon_0-1)^2 k_B T}{3(2\epsilon_0+1)\epsilon_0(2l+1)} \left\{ 2\epsilon_0 \left[ \frac{l}{(l+1)(l+2)D_R + \epsilon_0 \tau_D^{-1}} + \frac{l+1}{l(l-1)D_R + \epsilon_0 \tau_D^{-1}} \right] + \left[ \frac{l}{(l+1)(l+2)D_R + \tau_D^{-1}} + \frac{l+1}{l(l-1)D_R + \tau_D^{-1}} \right] \right\}. \tag{10}$$

In addition their theory included, for the first time, the effects of the intermolecular orientational correlations in the analysis of dielectric friction. This naturally led to the conclusion that translational diffusion can significantly decrease the magnitude of dielectric friction. In addition, Madden and Kivelson (1984) developed a successful three-variable theory of dielectric relaxation which can be considered as a generalization of the earlier three-variable theory of Guillot and Bratos (1977). The study of dielectric relaxation has two interesting limits, one is the underdamped and the other one being the overdamped. A liquid is said to be in the underdamped limit when the orientation and the angular momentum both relaxes at comparable rates so that the momentum relaxation cannot be neglected, whereas in the overdamped limit the angular momentum relaxation is much faster and can be safely ignored. Finally, a general theorem that attempts to establish a relation between the macroscopic orientational relaxation time, as measured by the dielectric relaxation experiments and the single particle orientational relaxation, was proposed. This macro–micro relation seems to be generally useful in the study of orientational relaxation in dipolar liquids.

The study of orientational relaxation in dipolar liquids has received a big boost recently because of the rapid advances in the study of ultra-fast solvation dynamics of charged species in dipolar liquids (Bagchi 1989, Maroncelli *et al.* 1989, Barbara and Jarzeba 1990, Fleming and Wolynes 1990, Bagchi and Chandra 1991, Carter and Hynes 1991, Raineri *et al.* 1992, 1993, 1994a, b, Resat *et al.* 1992, 1993, Maroncelli 1993, Alavi and Waldeck 1994, Gauduel and Rossky 1994, Hynes 1994). It was found that solvation of an ion and a dipole can proceed at a rate which is intimately connected with the rate of polarization relaxation as measured by dielectric relaxation and far infrared (fir) experiments. However, the situation in solvation dynamics is rather complex, as it requires a knowledge of not only the collective relaxation but also of the single particle orientational dynamics. In fact, one requires a knowledge of collective orientational relaxation at all length-scale (Bagchi 1989, Bagchi and Chandra 1991). Several detailed computer simulation studies have been carried out to explore the relationship between solvation dynamics and collective relaxation (Maroncelli 1993).

In our laboratory at the Indian Institute of Science, Bangalore, we have developed a molecular theory of orientational relaxation and solvation dynamics in dipolar liquids—some of our early results have already been reviewed elsewhere (Bagchi 1989, Bagchi and Chandra 1991). Our effort was different from the earlier studies in that it was based on a molecular hydrodynamic description which has been very successful in recent years to describe the complex dynamics of supercooled atomic liquids (Boon and Yip 1980, Götze and Sjögren 1987) For orientational dynamics, the molecular hydrodynamic approach was initiated first by Calef and Wolynes (1983). The main idea behind this approach is that in dense liquids, the density relaxation can become very slow because of the 'cage effects' due to the presence of strong orientational and spatial correlations. Therefore, a quantitative description of various relaxation processes may be obtained in terms of a set of extended hydrodynamic equations where the relaxation of momentum is described by a generalized Navier–Stokes equation that contains a 'mean-field' force term, derived from a local free energy functional—the latter is obtained from density functional theory (Munakata 1978, Ramakrishnan and Yussouff 1979, Bagchi 1989). The mean-field force term is proportional to the fluctuating density of the liquid. The advantage of this description is that is easily leads to a system of linear equations that contains both the effects of the intermolecular orientational correlations and the dissipation. As already mentioned, this description, which we refer to as molecular hydrodynamic, has been quite successful in explaining and systematizing a large body of experimental data on relaxation in dense and supercooled molecular liquids (Munakata 1978, 1985, Ramakrishnan and Yussouff 1979, Boon and Yip 1980, Kirkpatrick 1985, Rice *et al.* 1985, Götze and Sjögren 1987, Kawasaki 1995).

The above study revealed many interesting aspects of relaxation in dipolar liquids. It showed that single particle orientational relaxation can be strongly coupled to the collective relaxation and vice versa (Vijayadamodar *et al.* 1989), much in the same way as in the equations of relaxation for simple monatomic liquids (Boon and Yip 1980, Kirkpatrick 1985, Götze and Sjögren 1987). Our study showed that the translational modes can greatly accelerate the decay of collective orientational relaxation at the intermediate wave-vectors (that is $\mathbf{k} \geqslant 2\pi/\sigma$, where $\sigma$ is the molecular diameter) where the collective orientational relaxation is slow because of the presence of the intermolecular correlations. This in turn leads to a significant reduction in the magnitude of the dielectric friction experienced by a dipolar molecule (Vijayadamodar *et al.* 1989). If the equations for dielectric friction and dielectric relaxation are solved simultaneously, one finds an important hidden role of the translational modes in dielectric relaxation—the translational modes can make the dielectric relaxation Debye- like (Bagchi and Chandra 1990). The theory also predicts that the single-particle orientation in an overdamped liquid can have a slow long-time decay which originates from the local orientational correlations. In the underdamped limit, the theory also makes several predictions that appear to be quantitatively similar to the three-variable theory (Guillot and Bratos 1977, Madden and Kivelson 1984, McConnel 1991).

The molecular hydrodynamic theory has also been studied by several other groups (Wei and Patey 1990, Raineri and Friedman 1992) with rather similar conclusions.

There are, however, several important concepts and issues revealed by the theoretical studies that are not easy to test experimentally. For example, the role of translational modes in the orientational relaxation or, the rank dependence of the dielectric friction. In order to understand these important issues, we recently carried out detailed computer simulation studies of orientational relaxation in a dipolar lattice (Zhou and Bagchi 1992, Ravichandran and Bagchi 1994a, b, c, d). Because of the simplicity of the system, it was possible to carry out accurate simulations. These simulations allowed us to address several fundamental issues, (like the rank dependence of dielectric friction), directly. Especially revealing has been the detailed understanding of the reasons behind the inadequacy of the continuum model. Recently, molecular dynamics simulations of the dipolar lattice has also been carried out (Ravichandran and Bagchi 1994 b) to understand the role of correlations in the underdamped limit of orientational relaxation. These results have motivated us to carry out further theoretical studies, detailed below.

The broad objectives of this review are to understand and, wherever possible, to quantify the role of intermolecular correlations in orientational relaxation. That these are difficult objectives can be appreciated from the following. Theoretical studies have long suggested that dipolar correlations should be important and one of the signatures would be a marked non-exponentiality in the decay of the orientational time correlation functions. Thus, theories predicted that dielectric relaxation, even of a moderately polar dipolar liquid, should be markedly non-Debye. Experiments, on the other hand, have repeatedly demonstrated that most of the common dipolar liquids obey the Debye equation rather well. The well-known examples are water, acetonitrile, and methanol (Hasted *et al.* 1985, Barthel *et al.* 1990, 1991, Guillot *et al.* 1990) (the librational modes at high frequency are not the kind of signatures that we are discussing here). Non-Debye dielectric relaxation is, of course, well-known in polymeric systems, but there again the origin is different. However, for dipolar liquids, the differences between the theoretical predictions and the experimental results are not understood. These clearly indicate that the existing theories are inadequate in many respects. In a recent study one reason for the failure of the theories has been attributed to the neglect of the translational modes (Bagchi and Chandra 1990). This is, of course, only a part of the story. A deeper understanding of orientational relaxation in dipolar liquids will require systematic studies by many scientists as the problem has many complicated features. In this review we look at a few of them by carefully comparing the computer simulation results with the different theoretical predictions.

As discussed below, a simple system is chosen so that many of the complicating features can be eliminated. We find that one can indeed learn a great deal from such a study.

The organization of the rest of the review is as follows, In section 2, we discuss single-particle orientational relaxation and dielectric friction. In section 3 we consider the collective orientational relaxation and dielectric function. In section 4 a brief discussion on solvation dynamics is given. In section 5 the relation between the single-particle and the collective memory function has been presented. In section 6 we present the theoretical work on orientational caging using the molecular hydrodynamic theory. Section 7 concludes with a discussion of the results and our current status of understanding of orientational relaxation.

## 2. Single particle orientation and dielectric friction

Because the dipolar liquids often consist of molecules of rather complicated shapes, the understanding of the details of orientational motion of these molecules is a difficult task. Recently hydrodynamic calculations of rotational friction were done with realistic shapes of non-polar molecules (instead of approximating them as spheres or ellipsoids) and the results were quite satisfactory (Fleming 1986, Bagchi 1994). This gives the hope that we are probably not too far from getting a reliable hydrodynamic theory of rotational motion for non-polar molecules of complex shapes. The situation, however, is far less satisfactory for polar molecules. Here most of the calculations are still concerned with spherical molecules with point charges or point dipoles located at the centre of a sphere (with the exception of the work of Waldeck and coworkers (Alavi and Waldeck 1994) that we shall discuss later). Unfortunately, even for such simple model situations, our understanding, is not precise.

In this section, we shall review the most recent advances that have taken place in this field. Specifically, we want to focus on some key concepts which has existed, but not tested rigorously in the past.

### 2.1. *Test of the continuum models*

As discussed in the introduction, initial studies of the single-particle orientational relaxation were based on the continuum model, which consists of the following four ingredients. First, one assumes a relation between the correlation function $C_l(z)$ and the diffusion coefficient $\hat{D}_R(z)$, as given by equation (6). This is the generalized diffusion equation result. Second, a partition of the total rotational friction into a short-range friction (due to viscosity), $\hat{\zeta}_0$, and a frequency dependent friction due to long-range dipolar interactions, $\hat{\zeta}_{DF}(z)$, is made, as given by equation (8). Third, the continuum model is used to express $\hat{\zeta}_{DF}(z)$ in terms of $\epsilon(z)$, already given by equation (9). And lastly, a continuum model relation is derived between $\epsilon(z)$ and $\hat{C}_1(z)$. This expression is given by

$$\frac{\epsilon_0[\epsilon(z)-1][2\epsilon(z)+1]}{(\epsilon_0-1)(2\epsilon_0+1)\epsilon(z)} = \mathscr{L}\left[-\frac{\mathrm{d}C_1(t)}{\mathrm{d}t}\right], \tag{11}$$

when $\mathscr{L}$ denotes a Laplace transformation with respect to time with frequency $z$ as the conjugate Laplace frequency. Since $C_1(t)$ is already given by the generalized diffusion equation, we can now solve all the equations self-consistently to obtain both $\epsilon(z)$ and $\hat{\zeta}_{DF}(z)$—the two intermediate key quantities. Our reason for discussing the above steps in detail is to emphasize the assumptions that form the backbone of the continuum mode. Note that any one of these assumptions is not easily verifiable; even the experimental test of the overall prediction is difficult. In fact, a clear indication of the inadequacy has come only recently through the extensive work on solvation dynamics, (Bagchi 1989, Maroncelli *et al.* 1989, Barbara and Jarzeba 1990, Fleming and Wolynes 1990, Bagchi and Chandra 1991, Raineri *et al.* 1992, 1993, 1994a, b, Maroncelli 1993, Alavi and Waldeck 1994, Bagchi and Roy 1994, Hynes 1994). Even then it is not all obvious which of the above assumptions (if not all) are responsible for the breakdown of the continuum model. This is important because one does not expect the generalized diffusion equation to be seriously in error in the overdamped limit. So, we are left with the following alternatives, either equation (9) or equation (11) is in error, or even both may be erroneous.

In order to answer the above questions, detailed computer simulation studies of Brownian orientational dynamics of a dipolar lattice has been carried out (Papazyan and Maroncelli 1991, Zhou and Bagchi 1992, Zhou *et al.* 1992). In this system, the point dipoles are fixed at the sites of a simple cubic lattice. These dipoles interact through the usual dipole–dipole potential (Allen and Tildesley 1987), given by equation (4) of this review. The dipoles are free to undergo rotational Brownian motion in the force field of all other dipoles of the system. The dynamics in this simple model is described essentially by only one dimensionless parameter (or polarity) $\eta = \rho_0\mu^2/3k_BT$, where $\rho_0$ is the number density of the system and $\mu$, the magnitude of the dipole moment of a molecule.

The merit of simulating the Brownian dipolar lattice is that the separation of the total friction into a bare and dielectric ($\zeta_{DF}$) component is built into the system, $\zeta_0$ being supplied from outside. In addition, the system is in the overdamped limit which is also the usual assumption of the continuum limit. Another advantage is that we can test the assumptions of the continuum model part by part, supplying simulated functions whenever necessary. Another advantage of this simple model is that a perturbative treatment of both the single-particle and collective dynamics can be carried out using $\eta$ as the smallness parameter. This perturbative treatment was first carried out by Zwanzig (1963) and was further studied by several workers (Loring and Mukamel 1987, Zhou and Bagchi 1992, Roy and Bagchi 1994).

The equation of motion for the Brownian dynamics simulations can be conveniently written in the form of a first-order differential equation for its angular velocity ($\boldsymbol{\Omega}$).

$$\dot{\boldsymbol{\Omega}} = \beta D_R T_s(\boldsymbol{\Omega}) + \omega(t). \tag{12}$$

The random angular velocity is denoted by $\omega$. $D_R$ and $\omega$ are related by the fluctuation–dissipation theorem

$$\langle \omega(0) \cdot \omega(t) \rangle = 2D_R\delta(t), \tag{13}$$

where $D_R$ is the rotational diffusion coefficient and $\beta$ is $(k_BT)^{-1}$ and $T_s(\boldsymbol{\Omega})$ is the systematic angular torque.

Simulations have been performed with 257 and 515 dipoles. The trend for the reorientational correlation functions obtained from 515 dipoles is almost the same as that of 257 dipole system. This results discussed in this review correspond only to 257 dipole system.

As expected, the single-particle orientational correlation function unlike the collective correlation function, has a weaker size dependence. So, mostly, the single-particle orientational correlation function was calculated by following the trajectory of the central dipole in the system, in some cases, averaging has been done over the six nearest neighbouring sites of the central dipole for better statistics. Simulations have been performed at four different polarities ($\eta$ = (1/12), (1/6) (1/3), (1/2)). The time step of the simulation was chosen to be equal to 0·01 $D_Rt$. Equilibration was done over a time $4 \times 10^5$ $D_Rt$ and the averages have been collected over an interval of $6 \times 10^5$ $D_Rt$.

The values of the static dielectric constant ($\epsilon_0$) for the four polarities $\eta = (1/12)$, (1/6), (1/3), (1/2) are 2·5, 4·9, 12·0, and 19·0, respectively (Zhou *et al.* 1992). The required values of $\tau_D$ can be obtained from the integral of the simulated collective dipolar time correlation function. The collective moment was nearly exponential (and $\epsilon(\omega)$ Debye-like) till $\eta = 1/3$. And the deviation from exponentiality was not very large till $\eta = 1/2$ the latter is the highest polarity studied in this work. The values of $\tau_D$ for the four polarities were $\tau_D = 0{\cdot}7\, D_R^{-1}$ for $\eta = 1/12$, $\tau_D = 1{\cdot}0\, D_R^{-1}$ for $\eta = 1/6$, $\tau_D = 1{\cdot}5\, D_R^{-1}$ for $\eta = 1/3$ and $\tau_D = 1{\cdot}85\, D_R^{-}$ for $\eta = 1/5$ (Zhou *et al.* 1992).

The dielectric friction on the orientationaly fixed central dipole can be calculated using the expression (Hubbard and Wolynes 1978, Madden and Kivelson 1982, Madden and Kivelson 1984)

$$\hat{\zeta}_{DF}(z) = \frac{\beta}{2}\int_0^\infty dt \exp(-zt)\, C_N(t), \tag{14}$$

where $C_N(t$ is the torque–torque correlation function

$$C_N(t) = \langle N_1(0) N_1(t) \rangle, \tag{15}$$

and $N_1$'s are the time dependent fluctuating torques acting on the central dipole. The calculated dielectric friction has been used later in the theories considered for comparison with the simulation. The correlation time ($\tau_l$) defines the effective coefficient ($D_l^3$) through the following relation:

$$D_l^e = \frac{1}{l(l+1)}\frac{1}{\tau_l}, \tag{16}$$

with

$$\tau_l = \int_0^\infty dt\, C_l(t). \tag{17}$$

Table 1. Effective diffusion coefficients from the Brownian dynamics simulations and from the theories at different polarities.

| $\eta$ | | $D_1^e$ | $D_2^e$ | $D_3^e$ | $D_4^e$ | $D_5^e$ | $D_6^e$ |
|---|---|---|---|---|---|---|---|
| | NZ | 0·826 | 0·826 | 0·826 | 0·826 | 0·826 | 0·826 |
| | HW | 0·899 | 0·914 | 0·941 | 0·960 | 0·971 | 0·978 |
| 1/12 | MK | 0·861 | 0·920 | 0·954 | 0·971 | 0·979 | 0·986 |
| | SIMUL | 0·891 | 0·930 | 0·958 | 0·972 | 0·980 | 0·992 |
| | NZ | 0·635 | 0·635 | 0·635 | 0·635 | 0·635 | 0·635 |
| | HW | 0·768 | 0·799 | 0·852 | 0·893 | 0·922 | 0·941 |
| 1/6 | MK | 0·690 | 0·799 | 0·869 | 0·912 | 0·938 | 0·954 |
| | SIMUL | 0·700 | 0·810 | 0·887 | 0·916 | 0·933 | 0·940 |
| | NZ | 0·452 | 0·452 | 0·452 | 0·452 | 0·452 | 0·452 |
| | HW | 0·622 | 0·664 | 0·730 | 0·790 | 0·837 | 0·872 |
| 1/3 | MK | 0·506 | 0·631 | 0·719 | 0·787 | 0·837 | 0·873 |
| | SIMUL | 0·400 | 0·574 | 0·656 | 0·746 | 0·794 | 0·821 |
| | NZ | 0·382 | 0·382 | 0·382 | 0·382 | 0·382 | 0·382 |
| | HW | 0·540 | 0·584 | 0·651 | 0·718 | 0·774 | 0·818 |
| 1/2 | MK | 0·431 | 0·550 | 0·634 | 0·706 | 0·765 | 0·811 |
| | SIMUL | 0·179 | 0·316 | 0·455 | 0·526 | 0·641 | 0·700 |

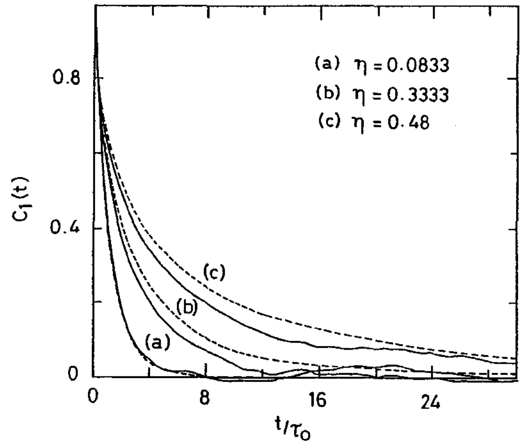


Figure 1. A comparison of the single-particle orientational correlation function from the Brownian dynamics simulation (solid curve) and from the generalized diffusion equation (dashed curves) using the dielectric friction from the Brownian dynamics simulation: (*a*) $\eta = 0{\cdot}083$: (*b*) $\eta = 0{\cdot}3333$: and (*c*) $\eta = 0{\cdot}48$. Note that the time is scaled by $\tau_0$.

The calculated values of the effective diffusion coefficients from the simulation are reported in table 1.

Next the results of the simulations are briefly discussed and compared with the continuum models and with the perturbative calculation.

We shall discuss first the validity of the continuum model expressions of the torque–torque correlation function ($C_N(t)$). In this comparison, the simulated dielectric function has been used so that one can test the accuracy of the form only, without any probable drawback from any approximate dielectric function. The simulation results show that the generalized diffusion equation (GDE) is rather accurate, as depicted in figure 1—the agreement is particularly good at low polarities. Note that here the dielectric friction is taken from simulation directly, so that we are strictly comparing the validity of GDE. Figure 2 shows the comparison between the continuum model prediction and the simulated $C_N(t)$. The continuum model predicts a much faster decay of $C_N(t)$ leads to an almost Debye like $\epsilon(\omega)$ in the continuum model.

The effective medium relation between $C_1(t)$ and $\epsilon(z)$ has also been tested. This has been done by using simulated $\epsilon(z)$ in the left hand side of equation (11). The comparison is shown in figure 3. Again, the continuum model theory fares badly.

Thus, the Brownian dynamics simulations of the dipolar lattice reveal the main limitations of the continuum mode. They show that both the effective medium expressions for $C_N(t)$ and $\epsilon(z)$ are inadequate even at moderate polarities. On the other hand, the generalized diffusion equation seems to fare well when a proper dielectric friction is supplied from outside. It is especially heartening to see that the slow decay of $C_1(t)$ is reproduced by the GDE.

For the Brownian lattice model, a simple perturbative expression for the orientational correlation function can be derived by using Zwanzig's projection operator technique. This expression, as a function of Laplace frequency $z$, is given by (Zhou and Bagchi 1992)

$$\hat{C}_1(z) = \frac{1}{z + (1/\tau_0)\{1 + R_1\eta^2[(1+\tau_0 z)^{-1} + \frac{1}{2}(4+\tau_0 z)^{-1}]\}^{-1}}, \tag{18}$$

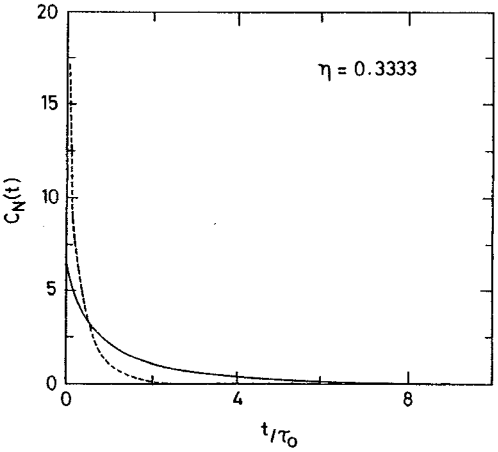


Figure 2. A comparison of the torque–torque correlation function from the Brownian dynamics simulation (solid curve) and from the continuum model (dashed curve) at $\eta = 0{\cdot}3333$. The time is scaled by $\tau_0$.

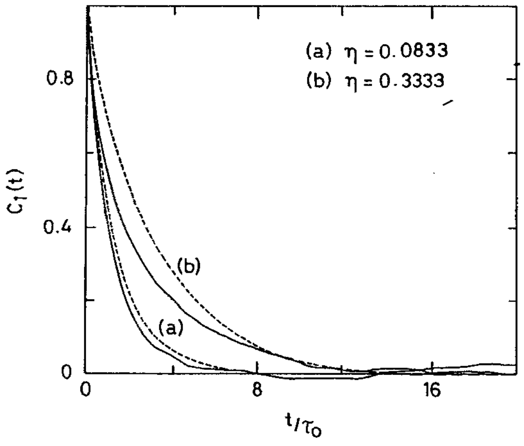


Figure 3. A comparison of the single-particle orientational correlation function from the Brownian dynamics simulation (solid curves) and from the effective-medium relation of the continuum model (dashed curves) using the dielectric function from the Brownian dynamics simulation: (*a*) $\eta = 0{\cdot}0833$ and (*b*) $\eta = 0{\cdot}3333$. The time is scaled by $\tau_0$.

where $R_1$ is an unaveraged lattice sum at site 1, equal to 1/3 1: $T_{11}^2$, $T_{ij}$ is the usual dipole dyadic tensor and $\tau_0 = (2D_R)^{-1}$. This expression is exact to the order of $\eta^2$. This fully microscopic expression agrees very well with the simulated results at low polarities, but fails to describe the slow long-time decay that develops at higher polarities, which is not surprising.

The perturbative treatment can also be used to understand the dielectric friction. Equation (18) gives the following expression for $\zeta_{DF}(z)$

$$\frac{\hat{\zeta}_{DF}(z)}{\zeta_0} = R_1\eta^2[(1+\tau_0 z)^{-1} + \tfrac{1}{2}(4+\tau_0 z)^{-1}], \tag{19}$$

where $R_1$ is a lattice sum. The Nee–Zwanzig continuum model, on the other hand, gives the following expression

$$\frac{\hat{\zeta}_{DF}(z)}{\zeta_0}=\frac{16\pi^2}{3}\eta^2(1+\tau_0 z)^{-1}. \tag{20}$$

For an infinite system, $R_1 = 16{\cdot}8$, whereas $16\pi^2/3 = 52{\cdot}6$. Thus, the continuum model predicts a value that is about three times larger than the perturbative treatment at all frequencies.

In section 5, we shall discuss a fully microscopic calculation of $C_1(t)$. This microscopic calculation based on a molecular hydrodynamic theory (Bagchi and Chandra 1991), provides a satisfactory description of orientational dynamics in the dipolar lattice.

### 2.2. *Rank dependence of the dielectric friction*

We next address the question of rank ($l$) dependence of the orientational relaxation in general and of dielectric friction in particular. According to Debye theory (1929), the rotational diffusion correlation functions $C_l(t)$ decay exponentially with a rate equal to $l(l+1)D_R$ and that the rotational diffusion coefficient has no dependence on the rank $l$. The generalized diffusion equation (equations (5) or (6)) makes the same assumption. Thus, the treatment of Nee and Zwanzig (NZ) (1970) totally neglected the rank dependence. It was Hubbard and Wolynes (1978) who first suggested that the rank dependence can be rather important in dipolar liquids and should decrease with $l$ for the following simple reason. As the rank $l$ increases, the relaxation of $C_l(t)$ becomes faster and the frictional retardation of the orientation motion due to dipolar interactions become less significant. This effect is particularly important in dipolar liquids because of the long-range nature of dipolar interactions which make the dielectric friction frequency dependent. Madden and Kivelson (1982) has also addressed the issue of rank dependence by using the Mori hierarchy (Boon and Yip 1980). Their expression for dielectric friction predicts a strong, rank $l$ dependence of the dielectric friction, which decreases with increasing $l$.

From a practical point of view, this $l$ dependence of dielectric friction can be useful to understand the difference between various correlation functions that are routinely measured in experiments. For example, $l = 1$ correlation function is accessible by dielectric relaxation measurements, whereas $l = 2$ function is measured by fluorescence depolarization, Raman and Kerr relaxation experiments. This intrinsic rank dependence of dielectric friction is sometimes ignored and the expression for $l = 1$ is used to interpret experiments that probe only the $l = 2$ correlation function (Dutt *et al.* 1991). An interesting example of the use of information from an $l = 2$ experiments to explain the results of an $l = 1$ level experiment is the ion solvation dynamics in acetonitrile (Cho *et al.* 1992)—the latter has been explained (Bagchi and Roy 1993, Roy *et al.* 1993) by using the Kerr relaxation data of Lotshaw and McMorrow (1991). However, such applications require a detailed understanding of the rank dependence of rotational friction.

Brownian dynamics lattice simulations show conclusively that the dielectric friction decreases rapidly with the rank $l$. This is shown in figure 4. These results are in qualitative agreement with the predictions of Hubbard and Wolynes (HW) (1978) and also of Madden and Kivelson (MK) (1982). In table 1, a comparison between the simulations and the various theories is shown for the rank dependent effective diffusion

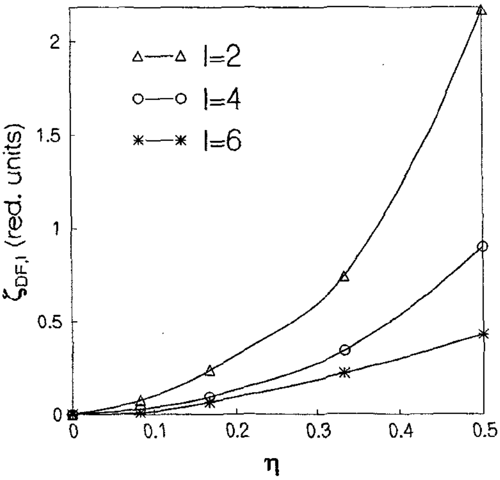


Figure 4. Values of the dielectric friction ($\zeta_{DF,l}(z = 0)$) obtained from the Brownian dynamics simulation plotted against polarity for different ranks. Note the above values of dielectric friction are scaled by the bare friction, $\zeta_0$.

coefficient, $D_l^e = k_BT/\zeta_0 + \hat{\zeta}_{DF,l}$). The theories of Hubbard and Wolynes (1978) and of Madden and Kivelson (1982) agree rather well with the simulation at low polarities; the predictions of the latter fare somewhat better. However, these theories seem to break down at higher polarities. The better agreement of Madden and Kivelson (1982) may be because this theory includes both the longitudinal and the transverse modes correctly, whereas only a composite rate is used in the theory of Hubbard and Wolynes (1978). The inadequacy of the molecular theory of Madden and Kivelson (1982) at high polarities is not well-understood at present, but may be partly due to the neglect of short-range intermolecular orientational correlations which are known to contribute significantly to dielectric friction (Vijayadamodar *et al.* 1989, Bagchi and Chandra 1990). This is a problem which requires a better understanding.

The observed rank dependence of dielectric friction certainly raises several questions—how important is this dependence for experimental situations? In order to answer this question further study is certainly required (and some will be detailed below), but it can be safely said that for nearly spherical and slow aprotic liquids like propylene carbonate and methyl iodide, this effect is expected to be non-negligible. This is because in the overdamped limit the magnitude of the dielectric friction scales with the short-range friction, $\zeta_0$.

Let us now discuss a few important points of experimental interest regarding the rank dependence. The rotational diffusion model (which is valid when diffusion occurs by small jumps) predicts that $\tau_1/\tau_2 = 3$, where $\tau_l$ is the relaxation time of $l$th order spherical harmonic $Y_{lm}[\Omega(t)]$. However, if the reorientation occurs by random long jumps, then the prediction is that $\tau_1/\tau_2 = 1$ (Kivelson and Miles 1988, Kivelson and Kivelson 1989). The ratio of $\tau_1/\tau_2$ is taken as an indication of the nature of the orientational dynamics. There are, however, several complications for slow dipolar liquids. First, the rotational diffusion coefficient itself can depend on the rank $l$ due to the non-Markovian effects mentioned above (Hubbard and Wolynes 1978, Ravichandran and Bagchi 1994a). This may give $\tau_1/\tau_2 > 3$. That this can really happen is shown in table 2 where this ratio, calculated via the same Brownian dynamics simulation

Table 2. The values of the relaxation time $\tau_1$ and $\tau_2$ (defined by equation (17)) as a function of the polarity ($\eta$-$\mu^2\rho_0/3k_BT$) of the medium. We have also shown the ratio $\tau_1/\tau_2$ in the last column.

| $\eta$ | $\epsilon_0$ | $\tau_D$ | $\tau_1$ | $\tau_2$ | $\tau_1/\tau_2$ |
|---|---|---|---|---|---|
| 1/12 | 2·5 | 1·4 | 0·56 | 0·179 | 3·13 |
| 1/3 | 12·0 | 3·0 | 1·25 | 0·290 | 4·31 |
| 1/2 | 19·0 | 3·7 | 2·79 | 0·527 | 5·29 |

(as discussed above) is presented. Note that the ratio can be significantly higher than 3 at high polarities. This is because the first-rank correlation function undergoes a relatively larger slowing down, due to the dipolar interactions, than the second-rank correlation function. This is a clear manifestation of the rank dependence of the dielectric friction.

However, experimentally one does seem to find values of $\tau_1/\tau_2$ which range between 3 and 1 (Gerschel 1984). In dense liquids, the rotation will certainly have a certain amount of small jump character—the situation can be different in the rigid medium. Thus, this appears to be a puzzling contradiction which we now address, although somewhat qualitatively.

There is one aspect of orientational relaxation which appears to have been overlooked in the past discussions on the ratio $\tau_1/\tau_2$. This is the fact that $C_1(t)$ is not directly available, and a measure of $\tau_1$ is usually taken from the dielectric relaxation time $\tau_D$ (Gerschel 1984)—although it has been pointed out that these two can be rather different (Maden and Kivelson 1984, Bagchi and Chandra 1991). Thus, in slow liquids, one should really compare $C_1(t)$ with $C_2(t)$. In the absence of such comparison, one must understand the relation between $\tau_1$ and $\tau_D$. This is again difficult because $C_1(t)$ can be non-exponential while dielectric relaxation can also be non-Debye. We can, therefore, compare only the average relaxation times, $\langle\tau_i\rangle$, with an assumed Debye-like relaxation of $\epsilon(z)$. Computer simulations indicate that in the absence of the translational modes, $\langle\tau_1\rangle$ can be larger than $\tau_D$ (see table 2). We then have the following inequalities,

$$\langle\tau_1\rangle \gtrsim \tau_D > \langle\tau_2\rangle.$$

Therefore, we may have the following scenario. For diffusive motion, $\tau_1/\tau_2$ can be significantly larger than 3, but $\tau_D/\tau_2$ can still be close to 3. Thus, replacing $\tau_1$ by $\tau_D$ may lead to wrong conclusion about the validity of the rotational diffusion model. The situation can be simpler at temperatures much above the freezing/melting point where the assumption $\tau_1 \simeq \tau_D$ may still be valid.

### 2.3. *Relaxation in the underdamped limit*

We next address an entirely different question on dielectric friction. What is the magnitude of this friction in the underdamped limit? This question is of considerable current interest because of the effort of relating the results of ultra-fast solvation dynamics experiments with the molecular relaxation observed by the optical Kerr effect (Cho *et al.* 1992, 1993, Roy *et al.* 1993). While solvation dynamics probes essentially the $l = 1$ orientational relaxation, the Kerr relaxation probes a complex dynamics which involve primarily $l = 2$ in the short time, although it may also contain certain amount of $l = 1$ contribution. Thus, it is important to understand this rank dependence in an underdamped liquid also.

In fact, the rank dependence of the orientational relaxation in the underdamped limit was studied by Fixman and Rider (1969) many years ago for an entirely different model—the model studied by them was a collisional Boltzmann equation. Fixman and Rider made an interesting prediction that while $C_1(t)$ may exhibit diffusive dynamics after a transient Gaussian decay, the second and higher-rank correlation functions may not exhibit any diffusive dynamics at all. That is, the decay of these correlation functions will be entirely Gaussian. This rather surprising prediction can be partly understood in terms of the rate of relaxation of these functions as we discussed earlier. The higher the rank of the correlation functions, the faster is the decay and the less is the frictional resistance from collisions.

A full molecular dynamics simulations of orientational relaxation in a dipolar lattice has recently been carried out (Ravichandran and Bagchi 1994b) to understand the role of dipolar interactions in the underdamped limit and also to verify the prediction of Fixman and Rider (1969).

A major motivation to study the problem of orientational relaxation using molecular dynamics simulations comes from the recent discovery of the Gaussian component in the solvation dynamics of an ion or a dipole in a polar liquid (Rosenthal *et al.* 1991). The understanding of this inertia-dominated solvation requires an understanding of the effects of dipolar interactions on both the collective and the single-particle orientational relaxation in the inertial limit. A particularly relevant question here is the relation between the $C_1(t)$ and the $C_2(t)$, as they partly reveal the connection between the dielectric and Kerr relaxation respectively (Roy and Bagchi 1993a, b, c). Another motivation is to understand the role of dielectric friction in the underdamped rotation of small molecules (Nakahara and Wakai 1992). Again these simulations also have been used to check the validity of the continuum models and to enhance our understanding in this area.

We briefly summarize below the technical details of the molecular dynamics (MD) simulations. A MD code has been developed for a system of rigid point dipolar cubic lattice (as discussed in Brownian dynamics simulations) with the centres of mass of the dipoles held fixed on the lattice sites. The dipoles interact through the dipole–dipole potential (see equation (4)).

The natural units of the present simulations are the length unit, $a$ (the lattice constant), the energy unit, $A$ and the time unit, $\tau_0$. The latter two quantities are defined as follows

$$A = \mu^2/3a^3, \quad \text{and} \quad \tau_0 = (I/A)^{1/2},$$

$I$ being the moment of inertia of a dipole. Thus, the dimensionless reduced time, temperature and energy are given by

$$t^* = t/\tau_0, \quad T^* = k_BT/A, \quad U^* = \langle W \rangle/NA,$$

where $\langle W \rangle$ is the mean value of the total energy of the system, $U^*$ is the energy per dipole and $N$ is the total number of dipoles in the simulation system. Also note that $T^*$ is inversely proportional to the polarity parameter $\eta$, which has been used in earlier studies (Papazyan and Maroncelli 1991, Zhou and Bagchi 1992, Ravichandran 1994a, b, c, Ravichandran *et al.* 1994). Note that all the results of molecular dynamics simulations presented in this review are expressed in terms of the reduced variables.

To check the system size dependence on the calculated quantities, a run was performed with $N = 515$ dipoles at $T^* = 2{\cdot}0$. As there was no significant difference in results between the 257 and 515 systems, calculations were continued on a 257 dipole

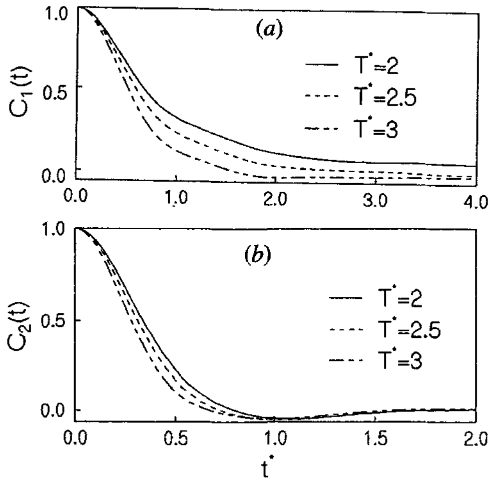


Figure 5. (*a*) The simulated (MD) single-particle orientational correlation function for $l = 1, C_1(t)$) is plotted against time at three different temperatures ($T^* = 2{\cdot}0$, $2{\cdot}5$, $3{\cdot}0$). Note that the time is expressed in reduced units. (See section: 2.3. for details). (*b*) The simulated single-particle orientational correlation function for $l = 2$ ($C_2(t)$) at three different temperatures. Note that the time is expressed in reduced units. (See section: 2.3. for more details).

system. Note that we are interested in the single-particle relaxation properties. Since this particle is chosen to be at the centre of the system, results converge easily and do not show any appreciable size dependence. In order to improve the statistics in the long time, averages were sometimes performed over the six dipoles that are nearest neighbours to the central dipole.

The rotational equations of motion were solved numerically by the leap-frog method proposed by Fincham (1981) with an integration time step of $\Delta t^* = 0{\cdot}00125$. Calculations were carried out at three different temperatures ($T^* = 2{\cdot}0$, $2{\cdot}5$, $3{\cdot}0$). Starting with random initial orientations of the dipoles, the system was equilibrated for $2 \times 10^6 \Delta t^*$ and averages were collected over $4 \times 10^6$ time steps at each temperature. For calculating the orientational correlation functions, a time length of $4 \times 10^6$ time steps have been used.

The dielectric friction on the orientationally fixed central dipole has been calculated using the relation (Nee and Zwanzig 1970, Hubbard and Wolynes 1978) given in equation (14) and (15). The calculated dielectric friction has been used later to obtain the $C_l(t)$'s from the memory function formalism, which will be discussed later in this section.

The rotational diffusion constant ($D_R$), defined by

$$D_R = \frac{1}{3}\int_0^\infty \mathrm{d}t \langle \omega(0) \cdot \omega(t) \rangle, \tag{21}$$

has been calculated. Here $\omega(t)$'s are the angular velocities. The calculated values of the rotational diffusion coefficient, $D_R$ for $T^* = 2{\cdot}0$, $2{\cdot}5$, $3{\cdot}0$ are $0{\cdot}3563$, $0{\cdot}5480$ and $0{\cdot}8393$, respectively.

In figure 5, the calculated single-particle orientational correlation functions for both $l = 1$ and $l = 2$ at three different temperatures are shown. While $C_1(t)$ exhibits a transition from a fast Gaussian-like to a slow exponential-like decay, the higher-rank

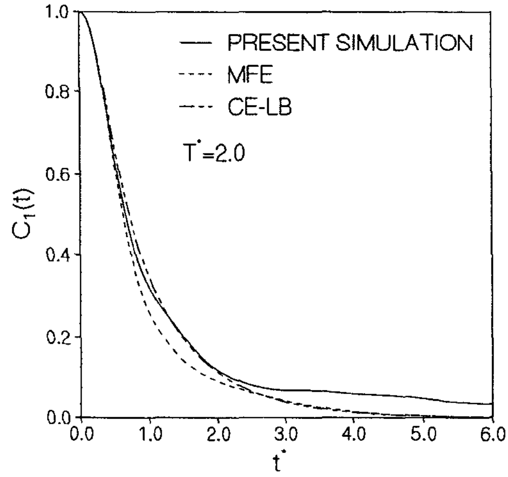


Figure 6. Single-particle orientational correlations obtained from the simulations are compared with the Lynden-Bell's cumulant expansion (CE-LB) and the memory function at temperature $T^* = 2{\cdot}0$. Note that the time and temperature are expressed in reduced units. (see section: 2.3. for more details).

correlation functions remain almost Gaussian throughout—in agreement with the prediction of Fixman and Rider (1969). The long-time tail indicates the importance of dielectric friction. The above results can be easily understood as follows. As the rank ($l$) increases, the decay becomes faster. Consequently, the relevant friction that could retard the relaxation of $C_l(t)$ for higher $l$ is only the high-frequency component of $\hat{\zeta}_{DF}(z)$. However, the value of this friction is small at large frequency and so is the role of dielectric friction for large $l$'s. This explains why the decay of $C_l(t)$ for $l \geqslant 2$ is mostly Gaussian—only the decay of $l = 1$ correlation function is sufficiently slow to face a large dielectric friction to make its decay diffusive. In the present case, the diffusion should really be described as a continuous time random walk (CTRW) for $C_l(t)$. Note that the diffusive decay of $C_1(t)$ sets in the long time. Thus, if one wants to coarse grain the dynamics to find the underlying CTRW, the jumps would be rather long. Therefore, for this model, dynamics can be described by small jumps only for $l = 1$ reorientation and not for $l \geqslant 2$ reorientations (Kivelson and Miles 1988).

Theoretical description of the short-time relaxation is usually simpler than that of the long-time part because simple expansion around $t = 0$ is often satisfactory. Lynden-Bell (1984) has derived a rather elegant expression for $C_l(t)$ by using the cumulant expansion technique. This expression is given by

$$\ln C_l(t) = -l(l+1)\langle\omega_x^2\rangle \int_0^t d\tau\,(t-\tau)C_\omega(\tau), \tag{22}$$

where $\langle\omega_x^2\rangle$ is the $x$-component of the mean square angular velocity and $C_\omega(t)$ is the angular velocity correlation function. Since $C_\omega(t)$ can be obtained from the molecular dynamics simulation, a complete test of equation (22) can be carried out. Such a comparison is shown for $C_1(t)$ in figure 6 which reveals that the cumulant expansion provides a satisfactory description of the relaxation at short times, but fails to capture the slow long-time decay of $C_1(t)$. This is, of course, expected.

An alternative approach that is commonly employed is to use the following memory function expression for $C_l(t)$

$$C_l(t) = \mathscr{L}^{-1}\left\{z + \frac{l(l+1)k_B T}{I[z + \hat{\zeta}_{DF}(z)]}\right\}^{-1}. \tag{23}$$

Since $\hat{\zeta}_{DF}(z)$ can be calculated directly from the molecular dynamics simulation, we can test equation (23). Figure 6 shows this comparison also. The short-time agreement is again good, but the long-time behaviour of equation (23) is wrong. This is somewhat surprising as we expected the memory function to provide a reasonable description in the long time, unlike the cumulant expansion which is restricted by definition to short-time dynamics.

The failure of the memory function description of underdamped relaxation at large polarities seem to have come from a fundamental drawback of such descriptions. In order to understand this drawback, let us first recall that in order to derive a simple memory function expression like equation (23), one needs to assume that the only slow collective variables are the density and the angular momentum of the tagged molecule. In a dense dipolar liquid, there are other slow collective variables are the density and the angular momentum of the tagged molecule. In a dense dipolar liquid, there are other slow collective variables, which are coupled to the single-particle relaxation. Therefore, one must extend the set of slow variables to include the collective hydrodynamic modes also. Such coupling between single-particle and collective dynamical variables is well-known in atomic liquids (Boon and Yip 1980, Hansen and McDonald 1986), but it has not been adequately addressed in the case of molecular liquids. When this coupling is included, the resulting expression for the single-particle orientational correlation function has an additional contribution, which has a structure (Bagchi, unpublished work) similar to the ones familiar in mode-coupling theory (Boon and Yip 1980). Although a detailed analysis of this approach has yet to be carried out, the observed slow decay of $C_1(t)$ may be attributed, at least partly, to the mode-coupling effects.

Since the initial decay of the single-particle reorientational correlation functions are Gaussian, a good measure of the rate of decay is given by the time correlation function ($C_l(t)$) to fall to $(1/e)$ of its initial value. These decay times can be defined as $\tau_l(1/e)$. In table 3, the decay times for the simulation are presented along with those of the two theories mentioned above (Lynden-Bell and the conventional memory function approach). It is clearly seen from the table that the decay times of the molecular dynamics simulation varies approximately as $[l(l-1)]^{1/2}$, which is expected on trivial grounds. This indicates that the rank dependence of dielectric friction is of little significance at short times. This is strikingly different from the observation in the overdamped limit (Ravichandran and Bagchi 1994a, c).

## 3. Collective dynamics: dielectric relaxation

Dielectric relaxation is the study of the time dependence of the total dipole moment correlation function. The total moment of the system is the sum over the dipole moments of all the molecules of the system. This is equal to the long wavelength (that is, the $\mathbf{k} = 0$) limit of the polarization. Hence, one expects that the dielectric relaxation can be described by using a molecular hydrodynamic approach (Bagchi and Chandra 1991).

Traditionally, dielectric relaxation has been studied in the two extreme limits of very fast and very slow momentum relaxation—the former is referred to as the underdamped and the latter as the overdamped limits of relaxation. It is rather amusing to note that these studies proceeded quite independently of each other and except perhaps in the

Table 3. The values of $\tau_l(1/e)$ (which is the time taken for $C_l(t)$ to fall to $1/e$) from the molecular dynamics simulation (Simul) and from the theories at three different reduced temperatures. ($T^*$ is defined in section 2·3. of the text).

| | | $\tau_l(1/e)$ | | |
|---|---|---|---|---|
| $T^*$ | $l$ | Simul | CE-LB | MFE |
| | 1 | 0·613 | 0·677 | 0·564 |
| 2 | 2 | 0·299 | 0·327 | 0·285 |
| | 3 | 0·219 | 0·223 | 0·194 |
| | 4 | 0·167 | 0·170 | 0·152 |
| | 1 | 0·515 | 0·558 | 0·469 |
| 2·5 | 2 | 0·278 | 0·290 | 0·250 |
| | 3 | 0·201 | 0·200 | 0·174 |
| | 4 | 0·151 | 0·149 | 0·134 |
| | 1 | 0·446 | 0·491 | 0·416 |
| 3·0 | 2 | 0·246 | 0·258 | 0·227 |
| | 3 | 0·182 | 0·183 | 0·156 |
| | 4 | 0·143 | 0·150 | 0·129 |

work of Madden and Kivelson (1984), hardly any attempt has been made in the past to treat them in a unified way. The overdamped limit was treated, following the original treatment of Debye, by using the diffusion equation approach. On the other hand, the dielectric relaxation in the underdamped limit was assumed to occur by individual motion of independent dipolar molecules, that is, the collective effects were usually ignored. In this review, we briefly describe some of the recent work (Bagchi and Chandra 1990, Zhou and Bagchi 1992, Bagchi and Chandra 1993) on dielectric relaxation in both the limits.

When the effects of intemolecular interactions are included consistently, the molecular hydrodynamic theory predicts a surprisingly rich dielectric behaviour. The most notable among them is perhaps the 'hidden' role of the translational modes in making the dielectric relaxation Debye-like. Another important finding is the notable role of intermolecular interactions even in the underdamped dielectric relaxation.

In figure 7 we show theoretically predicted dielectric relaxation behaviour presented in a Cole–Cole plot (where the imaginary part of the frequency dependent dielectric function is plotted against the real part) for various values of a dimensionless dynamic quantity $p = D_T/(2D_R\sigma^2)$ where $D_T$ and $D_R$ are the translational and rotational diffusion coefficients of the liquid and $\sigma$ is the molecular diameter. The parameter, $p$ is a measure of the relative contribution of the translational modes to the collective orientational relaxation. The predicted dielectric relaxation (Bagchi and Chandra 1990) is markedly non-Debye in the absence of the translational modes of the liquid but it becomes Debye-like in the presence of a significant translational contribution. However, these results are somewhat biased towards non-exponential decay because the collective rotational dissipative kernel was replaced by the single-particle rotational friction. In order to further understand the role of intermolecular correlations, we investigated the dielectric relaxation of a Brownian dipolar lattice (Zhou and Bagchi 1992) where the dipoles are fixed in the lattice sites (therefore, the translational modes are absent) but allowed to undergo rotational Brownian motion while interacting with all the other dipoles of the lattice. It was found that the time dependence of the total moment

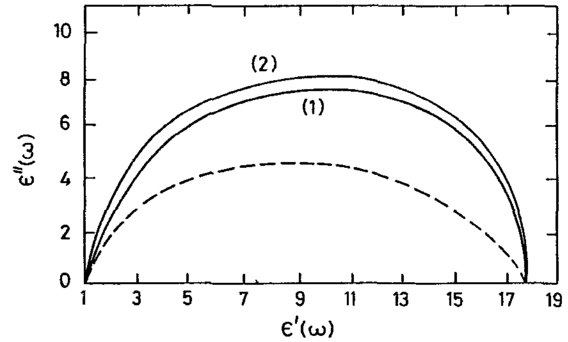


Figure 7. The Cole–Cole plot of the frequency dependent dielectric function, $\epsilon(\omega)$. In this plot the imaginary part, $\epsilon''(\omega)$, of the dielectric function is plotted against the real part, $\epsilon'(\omega)$. The Cole–Cole plot is shown for several values of the dimensionless parameter $p( = D_T/2D_R\sigma^2)$, where $D_T$ and $D_R$ are the translational and rotational diffusion constants of the dipolar liquid. The dashed curve is for $p = 0$ which means translational motion of the liquid molecules are frozen. Curves marked (1) and (2) are for $p$ equal to 0·05 and 0·25, respectively. The values of the static dielectric constant and reduced density are equal to 18 and 0·8, respectively. It can be seen from this figure that dielectric relaxation can be strongly non-Debye in the absence of the translational contribution, but may become Debye-like when translational contribution is significant. This figure is taken from Bagchi and Chandra (1990).

correlation function was again non-exponential with a slow long-time decay in agreement with the theory (Bagchi and Chandra 1990) where it was suggested to arise from the nearest-neighbour interaction. However, the effect was smaller than predicted by the theory.

In order to understand why the translational modes reduce the effects of local correlations, we have to understand the length dependence of orientational correlations. In the presence of strong orientational correlations among the nearest-neighbour molecules, the orientational relaxation of individual molecules slows down because of increased dielectric friction—the latter draws a large contribution from the nearest-neighbour molecules. However, if the molecules have large translational mobility, then the effects of the nearest-neighbour correlations decrease because translational motion is particularly effective in accelerating the rates of molecular length-scale density relaxation (Bagchi 1989, Bagchi and Chandra 1990, Bagchi and Chandra 1991). This in turn reduces the magnitude of the dielectric friction.

In the underdamped limit, the theoretical description is somewhat simpler because only the short-time behaviour of the dissipative kernels are required. Since the short-time behaviour is dominated by the static, intermolecular correlations, it is straight-forward to calculate this behaviour (Boon and Yip 1980), Note that in many earlier treatments of the high-frequency dielectric relaxation, only the single-particle rotational contributions were considered—the collective effects were left out. The role of these collective effects were made clear recently by Nitzan and coworkers (Neria *et al.* 1991, Neria and Nitzan 1992) who presented a detailed computer simulation of dielectric relaxation in model Stockmayer liquid (where molecules interact via a Lennard-Jones plus a point dipolar interaction) (Payne *et al.* 1993). This liquid can be in the extreme underdamped limit of momentum relaxation because dipolar interactions provide the only frictional resistance to the rotational motion. It was observed that the initial relaxation of the total dipole moment was a Gaussian function of time, as

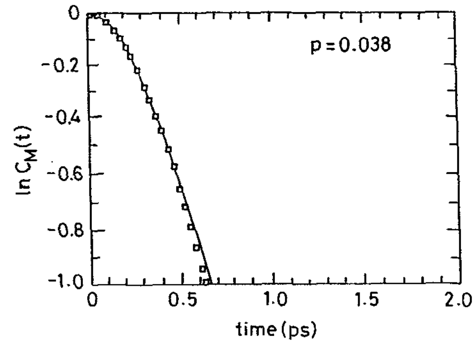


Figure 8. Comparison between the calculated total moment correlation function, $C_M(t)$ (solid line) and the simulated function (Neria *et al.*) (squares) for the model Stockmayer liquid. The translational parameter used is $p = 0{\cdot}038$. The details of the parameters used are as follows. Reduced density, $\rho^*(=\rho\sigma^3) = 0{\cdot}81$, reduced dipole moment, $\mu^*$ $(=\mu^2/k_BT\sigma^3) = 1{\cdot}32$, reduced temperature $T^*(=k_BT/\epsilon) = 1{\cdot}23$ and reduced moment of inertia, $\mathbf{I}^*(=I/m\sigma^2) = 0{\cdot}038$. Here $\sigma$ is molecular diameter, $m$ is the mass of the solvent molecule, and $\epsilon$ is the usual Lennard-Jones energy parameter. Note that no adjustable parameter has been used to calculate the theoretical curve. The calculational steps have been discussed in detail by Bagchi and Chandra (1992).

expected, but at a rate which was significantly different from the free inertial decay. The observed relaxation behaviour can be explained very well from the molecular theory (Bagchi and Chandra 1993). In figure 8 we show the agreement between the theory and simulation results for the time dependence of the total moment correlation function. The agreement is excellent. As discussed in Bagchi and Chandra (1993), such good agreement is possible because it is the free energy, rather than the dissipative kernel, that determines collective orientational relaxation in the short time. Therefore, it is the static equilibrium pair correlations, rather than the dynamics, that determine the initial decay.

A question that has been repeatedly asked in the problem of underdamped dielectric relaxation is the existence of collective excitations in the polarization relaxation (Lobo *et al.* 1973, Ascarelli 1976, madden and Kivelson 1984, Bagchi and Chandra 1990). The molecular theory predicts that such collective excitations are more likely to be observed in experiments that measure the longitudinal polarization relaxation (such as the solvation dynamics of an ion) than in experiments that measure the transverse relaxation, such as the dielectric relaxation. This can be understood from the expressions for the force constants of polarization fluctuation, as given by the following expressions (Chandra and Bagchi 1991)

$$K_L(\mathbf{k}) = \frac{2}{(2\pi)^2}\frac{\epsilon_L(\mathbf{k})}{\epsilon_L(\mathbf{k})-1}, \tag{24}$$

$$K_T(\mathbf{k}) = \frac{2}{(2\pi)^2}\frac{1}{\epsilon_T(\mathbf{k})-1}, \tag{25}$$

where $\epsilon_L(\mathbf{k})$ and $\epsilon_T(\mathbf{k})$ are the longitudinal and transverse dielectric functions (Bagchi and Chandra 1991, Madden and Kivelson 1984), respectively. In the long wavelength, that is, in the $\mathbf{k} \to 0$ limit), the force constant for longitudinal fluctuation is much larger than that for the transverse fluctuation. This is the reason why a collective excitation is possible for the longitudinal polarization.

Lastly, it should be pointed out that the hydrodynamic theory treats both the overdamped and the underdamped dielectric relaxation within the same hydrodynamic approach which, therefore, offers a unified description.

## 4. Solvation dynamics

By solvation dynamics one usually means the time dependence of the solvation energy of a newly created charged species in a dipolar liquid. In experiments this is measured most conveniently by following the time dependence of the Stokes shift of fluorescence from the charged probe—the fluorescence undergoes a continuous red shift with time. The solvation dynamics is usually represented in terms of the following function

$$S(t)=\frac{E_{\mathrm{solv}}(t)-E_{\mathrm{solv}}(\infty)}{E_{\mathrm{solv}}(0)-E_{\mathrm{solv}}(\infty)}, \tag{26}$$

where $E_{\mathrm{solv}}(t)$ is the time-dependent solvation energy which may be proportional to the average frequency of the fluorescence spectrum at time $t$. As a result of the remarkable advances in the laser spectroscopy and the related ultra-fast techniques, several exciting experiments (Kosower and Hupert 1986, Barbara and Jarjeba 1988a, b, Simon 1988, 1990, Maroncelli *et al.* 1989, Fleming and Wolynes 1990, Weaver and McManis 1990, Barbara *et al.* 1992, Gauduel 1992, Maroncelli 1992, Rossky and Simon 1994) have been performed recently which measured the time dependence of the function $S(t)$. In this account, we focus on a few fundamental theoretical questions that we shall attempt to understand. The present scenario, as we discuss below, is rather encouraging.

Let us first briefly summarize the continuum model predictions (Bakshiev 1964, Bakshiev *et al.* 1966, Mazurenko and Bakshiev 1970, Bagchi *et al.* 1984, 1989, Van der Zwan and Hynes 1985). When the dielectric relaxation of the dipolar solvent is a single exponential in time with $\tau_D$ as the (Debye) relaxation time, then the continuum model predicts that the solvation dynamics is also single exponential both for an ion and a dipole with slightly different time constants ($\tau_s$), given below.

For an ion

$$\tau_s=\frac{\tau_D}{\epsilon_0}, \tag{27}$$

For a point dipole

$$\tau_s=\frac{2\epsilon_\infty+1}{2\epsilon_0+1}. \tag{28}$$

Experiments and computer simulations have shown that the continuum model fails to describe the essential features of the solvation dynamics. For example, the solvation correlation function $S(t)$ can be strongly non-exponential even when the dielectric relaxation is single exponential, in particular that the solvation correlation function can exhibit rich and interesting behaviour is not even anticipated in the continuum models. This richness can be attributed to the fact that solvation dynamics probes the details of intermolecular correlations neglected in the continuum model, as discussed in the previous sections.

Two rather different types of molecular theories have been put forward to explain the experimental findings. In one approach, pioneered by Wolynes (Wolynes 1987), the well-known mean spherical approximation (MSA) model for ion solvation (Chan *et al.*

1979) was generalized to the time domain. This theory was subsequently expended greatly (Nichols III and Calef 1988, Rips *et al.* 1988a, b) and has been applied to analyse experimental and computer simulation results, with considerable success (Maroncelli 1993). This is certainly the easiest molecular theory for applications. There are essentially two drawbacks of the MSA. (i) It is not clear how to include the effects of the translational modes of the solvent in the solvation dynamics. (ii) It is not easily extendable beyond MSA which is reliable only for weakly polar dipolar liquids.

The second approach is based on the molecular hydrodynamic equation mentioned earlier. Here the time-dependent solvation energy of an ion is assumed to be given by the following expression (Calef and Wolynes 1983, Bagchi 1989, Bagchi and Chandra 1991)

$$E_{\rm solv}(t) = -\frac{1}{2}\int d\mathbf{r}\mathbf{E}_0(\mathbf{r})\cdot\mathbf{P}(\mathbf{r},t), \qquad (29)$$

where $\mathbf{E}_0(\mathbf{r})$ is the bare electric field of the ion and $\mathbf{P}(\mathbf{r},t)$ is the time-dependent solvent polarization induced by the ion-position $\mathbf{r}$ of the solvent molecule being measured from the centre of the ion. The latter is assumed to be immobile. Although, in principle, it is possible to include the effects of the solute ion on solvent dynamics (and this has been discussed in Chandra and Bagchi (1989)), most of the theoretical studies have assumed pure solvent dynamics for $\mathbf{P}(\mathbf{r},t)$. Under this approximation, it is convenient to work in the Fourier space using $\mathbf{k}$ as the wave-vector conjugate to the position $\mathbf{r}$. From the molecular hydrodynamic theory, one can derive the a simple relation for the wave-vector and frequency dependent longitudinal polarization (Roy and Bagchi 1993a). This subsequently leads to the following equation for the time dependent solvation energy (Roy and Bagchi 1993a)

$$E_{\rm sol}(t) = -\frac{Q^2}{\pi\sigma}\int_0^\infty dk\left[\frac{\sin(\mathbf{k}r_c)}{\mathbf{k}r_c}\right]^2\left[1-\frac{1}{\epsilon_L(\mathbf{k})}\right]\frac{1}{z+\Sigma(\mathbf{k},z)}, \qquad (30)$$

where $\Sigma(\mathbf{k},z)$ is the generalized rate of solvent polarization relaxation and is given by

$$\Sigma(\mathbf{k},z) = \frac{2f_L(\mathbf{k})}{\tau_I^2[z+\Gamma_\Omega(\mathbf{k},z)]} + \frac{pq^2 f_L(\mathbf{k})}{\tau_I^2[z+\Gamma_T(\mathbf{k},z)]}. \qquad (30a)$$

Here, $Q$ is the charge of the nascent ion being solvated. $\tau_c$ denotes the distance of closest approach between the solute ion and a solvent molecule. If the ion and the solvent are assumed to be spherical with diameters equal to $2r_{\rm ion}$ and $\sigma$, respectively, then $r_c = (1/2)(2r_{\rm ion}+\sigma)$. $\tau_I = (I/k_BT)^{1/2}$ is the inertial time constant of rotation of the solvent molecules having an average moment of inertia $I$. The static orientational correlations between the solvent molecules are presented by the quantity $f_L(\mathbf{k})$ where $f_L(\mathbf{k}) = 1 - (\rho_0/4\pi)c(110;\mathbf{k})$. Here, $\rho_0$ is the average number density of the dipolar liquid and $c(110,\mathbf{k})$ is the (110) component of the solvent two particle direct correlation function in the intermolecular frame (Gray and Gubbins 1984). The other static quantity that appears in the above set of equations is the wave-vector dependent longitudinal dielectric function, $\epsilon_L(\mathbf{k})$. This is, in turn, related to $f_L(\mathbf{k})$ as

$$1-\frac{1}{\epsilon_L(\mathbf{k})} = \frac{4\pi\eta}{f_L(\mathbf{k})}. \qquad (30b)$$

In equation (30*a*) $p$ is the solvent translational parameter defined earlier and signifies the relative importance of the translational modes of the solvent molecules in the polarization relaxation.

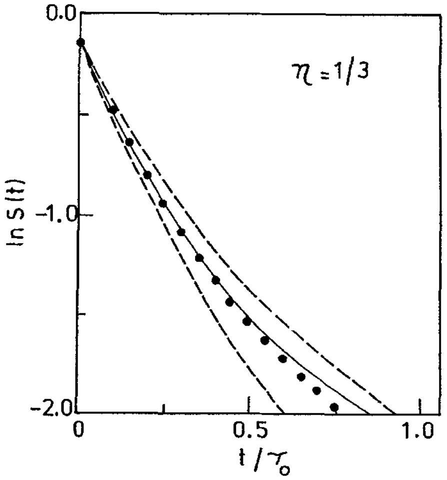


Figure 9. The time dependence of the solvation energy time correlation function $[S(t)]$ of an ion in the Brownian dipolar lattice of polarity $\eta = 1/3$. The molecular hydrodynamic calculation with memory effects is shown by the solid line and the computer simulation results by solid circles. The prediction of the Fried–Mukamel theory is shown by the dash–dotted line and that of the Markovian hydrodynamic theory (as reported by Zhou *et al.* (1992)), by the dashed line. Note that the time is scaled by $\tau_0$.

The dissipative dynamics of solvent are incorporated in the rate of polarization relaxation by the quantities, $\Gamma_\Sigma(\mathbf{k}, z)$ and $\Gamma_T(\mathbf{k}, z)$ which are termed as the rotational and the translational dissipative (or memory) kernels, respectively. These functions account for the momentum dissipation through intermolecular interactions, for example by collisions, as they are akin to the friction coefficients that resist the motion of a molecule in dense liquids. The dissipative kernel in the two extreme cases of long wavelength (that is in the $\mathbf{k} \to 0$) limit and small wavelength (that is in the $\mathbf{k} \to \infty$) can be easily obtained by computer simulations or theoretically. Since we know very little about the dependence of $\Gamma_R(\mathbf{k}, z)$ in the intermediate $\mathbf{k}$ region, the following phenomenological for has been proposed (Komath and Bagchi 1993)

$$\Gamma_R(\mathbf{k}, z) = \Gamma_s(z) + \frac{\Gamma_c(z) - \Gamma_s(z)}{1 + (k\sigma)^2} \tag{31}$$

where $\Gamma_s(z) = \hat{\zeta}(z) = \Gamma_R(\mathbf{k} \to \infty, z)$ (the single-particle limit) and $\Gamma_c(z) = \Gamma_R(\mathbf{k} = 0, z)$ (the collective limit). This has the correct limiting and the low $\mathbf{k}$ behaviour. Note that the above expression uses both the single particle and the collective friction coefficients.

Equations $30(a, b)$ have been used to calculate solvation dynamics in both the overdamped and the underdamped limit. We remind the reader that a liquid is said to be in the underdamped limit when the orientation and the angular momentum both relaxes at comparable rates so that the momentum relaxation can not be neglected. Thus, this is the opposite limit of that treated in Brownian dynamics. Here we shall present comparisons only with recent computer simulations because such comparisons are precise.

First, let us present the results for the overdamped limit. In this case the system is a Brownian dipolar lattice which has been discussed earlier. The solvation is non-exponential (Komath and Bachi 1993). The agreement between theory and simulation is remarkable. It is important to note that no adjustable parameter has been

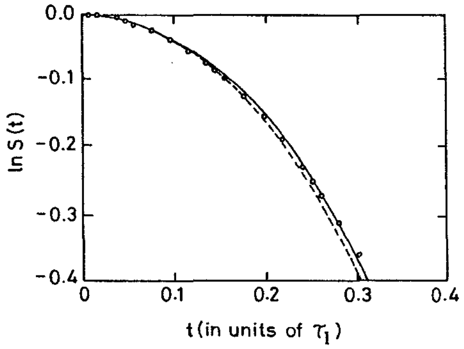


Figure 10. The comparison between the three theories of solvation dynamics in an underdamped Stockmayer liquid. Here we plot the solvation time correlation time, $S(t)$, for the situation when both the solute ion and the solvent molecules are translationally frozen, that is $p = 0{\cdot}0$ for solvent. The solid line represents the molecular hydrodynamic theory (MHT), while the dashed line corresponds to the dynamic mean spherical approximation (DMSA). The results of the memory function theory (MFT) of Fried and Mukamel are indistinguishable from MHT and therefore, have not been shown separately. The simulation results are shown by circles. The latter compare extremely well with the theoretical predictions. The other system parameters are the same as in figure 8 of this review. This figure has been taken from Roy and Bagchi (1993a).

used to generate the theoretical results shown in this figure 9, the rotational kernel has been calculated by using the molecular hydrodynamic equations given above. Moreover, the results from Fried and Mukamel (1990) and the hydrodynamic theories both give virtually indistinguishable results (Komath and Bagchi 1994) although the inputs for the two theories are quite different.

Solvation dynamics in underdamped liquids is currently a subject of great interest. Computer simulations (Maroncelli and Fleming 1988, Carter and Hynes 1991, Fonseca and Ladanyi 1991, Maroncelli 1991, Neria and Nitzan 1991, Papazyan and Maroncelli 1991, Perera and Berkowitz 1992, Maroncelli 1993, Maroncelli *et al.* 1994) and experiments (Rosenthal *et al.* 1991) have shown that the solvation in an underdamped liquid is *biphasic* with the two phases showing very different characteristics. The solvation starts with an ultra-fast component which decays in a few tens of femto seconds with a Gaussian time dependence. This part contributes about 60–80% to the total solvation. This is followed by a slow, exponential-like decay which carries the rest of the strength. Computer simulations and theoretical studies further suggest that the latter can be attributed to diffusive relaxation processes involving primarily the nearest-neighbour molecules. On the other hand, the nature of the ultra-fast component is somewhat controversial as to different explanations (Cho *et al.* 1992, Chandra and Bagchi 1991a, b, Roy and Bagchi 1993b, 1994) have been put forward. Cho *et al.* (1992) suggested that the initial Gaussian ultra-fast decay can be explained in terms of unphasing of independent oscillators provided a correct distribution of force constants of these oscillators is used. These results could provide a unified description of the Kerr relaxation and solvation dynamics experiments. A different interpretation has been put forward by Chandra and Bagchi (1991a, b), who suggest that the ultra-fast component arises primarily from the underdamped relaxation in a macroscopic potential whose force constant is given by the $\mathbf{k} = 0$ limit of equation (24). We shall come back to this interpretation again after we discuss the results.

In figure 10 we compare the results of the hydrodynamic theory with the computer simulation studies of Neria and Nitzan (1992). Here the system is the model Stockmayer liquid. The solvation dynamics in this system is quite different from what is observed in the overdamped limit—much of the decay can be well described by a Gaussian function of time. Here again the theoretical curve has been generated without any adjustable or external parameter. The agreement is truly amazing. The reason for such a good agreement is that the system is weakly polar so that static correlation functions provided by MSA (Wertheim 1971) are quite accurate. In this case also, Fried–Mukamel and the hydrodynamic approach led to almost identical results (Roy and Bagchi 1993a). It is note-worthy that the dynamic mean spherical approximation (Wolynes 1987, Nichols and Calef 1988, Rips *et al.* 1988a, b) also gives almost identical agreement with the simulation, as also shown in figure 2. of (Roy and Bagchi 1993a).

The above comparisons between simulation and theory clearly demonstrate that we have achieved a certain degree of understanding about the mechanism of solvation dynamics in simple dipolar liquids. They also answer several important questions. Firstly, it is clearly that in the absence of any specific solute–solvent interactions, solvation dynamics probes the unperturbed or natural motion of the solvent. Thus, in the language of statistical mechanics, the response of the solvent is linear. Secondly, in the absence of the translational modes, the solvation dynamics is highly non-exponential—precisely as predicted by the theory. More importantly, this non-exponentiality is a consequence of the local or short-range correlations present in a dense dipolar liquid. The translational modes reduce the effects of the local correlations by accelerating their decay, which may often be significant. Thirdly, in an underdamped liquid, the molecular theory presents the following scenario for the ultra-fast Gaussian solvation. In the short time, the dynamical response is inertial, especially in Stockmayer liquid where molecules are spherical and the only retarding friction is the dielectric friction. The relaxation is further accelerated because the relevant motion is collective which relaxes under the influence of a collective potential whose force constant, given by equation (24), is rather large for the long-wavelength modes. This explains why an underdamped relaxation can be indeed proceed at an astronomically fast speed. However, the explanation of the observed results in acetonitrile (McMorrow and Lotshaw 1991, Rosenthal *et al.* 1991, Cho *et al.* 1992, Roy *et al.* 1993) can be more involved. This is clearly a very interesting study for further work.

## 5. Relation between single-particle and collective memory function

In this section, we address the relationship between the single-particle and the collective orientational correlation functions. These correlation functions in turn are dependent on the memory functions. In order to make the discussion more quantitative, let us define two rather different orientational correlation functions—one for the single particle as

$$C^s_{lm}(t) = \langle Y^*_{lm}[\boldsymbol{\Omega}(0)] Y_{lm}[\boldsymbol{\Omega}(t)]\rangle, \tag{32}$$

and the other for collective as

$$C_{lm}(\mathbf{k}, ,\mathrm{t}) = \langle Y^*_{lm}(\mathbf{k}, 0) Y_{lm}(\mathbf{k}, t)\rangle, \tag{33}$$

where

$$Y_{lm}(\mathbf{k}, t) = \sum_{\alpha=1}^{N} Y_{lm}[\boldsymbol{\Omega}_\alpha(0)] \exp[i\mathbf{k}\cdot\mathbf{r}_\alpha(t)], \tag{34}$$

and $Y_{lm}(\Omega)$ are the spherical harmonics of rank $l$ and projection $m$. The sum in equation (34) runs over all the molecules of the liquid. As usual, **k** is the wave-vector conjugate to the position **r**.

On rather general grounds, these correlation functions can be represented in terms of their respective memory functions as follows (Madden and Kivelson 1982, Bagchi *et al.* 1990)

$$C^{s}_{lm}(z) = \left[z + \frac{l(l+1)k_{\mathrm{B}}T}{\hat{\zeta}(z)}\right]^{-1}, \tag{35}$$

$$C_{lm}(\mathbf{k}, z) = \left[z + \frac{l(l+1)f(llm;k)}{\Gamma(\mathbf{k}, z)}\right]^{-1}, \tag{36}$$

where $z$ is the Laplace frequency conjugate to time $t$ and $\hat{\zeta}(z)$ and $\Gamma(\mathbf{k}, z)$ are the memory functions for the single-particle and the collective angular momenta relaxation, respectively. In the expression for the collective orientational correlation function, $f(llm, \mathbf{k})$ is related to the orientational pair correlation function that represents the orientational pair correlation function that represents the orientational caging and its precise form will be discussed in the next section. $k_{\mathrm{B}}T$ is the Boltzmann constant times the absolute temperature. The memory function for the single-particle motion may be equated with the friction, but not with the collective one which may be significantly different—the definitions of these quantities will be made precise later. Clearly, in order to obtain the correlation functions, we need the memory functions. The first-principles calculations of these functions are extremely difficult and have not yet been done for any realistic system. This reason alone has made our understanding of orientational relaxation imprecise.

Recently, a detailed microscopic theory of orientational relaxation in dense molecular liquids has been developed where a self-consistent treatment of the single particle and collective orientational relaxation was presented (Bagchi and Chandra 1990, 1991, Chandra and Bagchi 1989b, 1990). The merit of this formalism is that the local orientational and spatial correlations were treated properly. This theory was applied to study solvation dynamics both in the slow (that is, overdamped) liquids (Bagchi 1989, Chandra and Bagchi 1989*d*) and the fast (underdamped, inertia dominated) liquids (Roy and Bagchi 1993, Roy *et al.* 1993). However, the theoretical calculations for orientational relaxation could not be pushed to a proper conclusion for the following reason. In order to carry out the full calculation of the dielectric friction, we need the full wave-vector and frequency dependent collective memory function. As mentioned earlier, it was not possible to calculate this quantity. Thus, a full self-consistent calculation could not be done in the past.

The situation has improved somewhat recently. Although it is still not possible to calculate the full collective memory function, there is now a reliable method to obtain this quantity directly from experiment in the zero wave-number limit (Bagchi and Roy 1993, Roy and Bagchi 1993a,b, Roy *et al.* 1993). In this method the molecular hydrodynamic equations are used to obtain a microscopic expression for the wave-vector and frequency dependent dielectric function in term of, among other functions, the collective memory function. Then the long wavelength limit of this relation can be used to express the collective memory function in terms of the frequency dependent dielectric function—the latter can now be obtained from the dielectric experiments (Bagchi and Roy 1993, Roy and Bagchi 1993a, b, Roy *et al.* 1993). *This is an exact procedure.* The sole limitation is that it gives only the long wavelength limit of the collective memory function. So, as a first approximation, one replaces the wave-vector dependence of the collective memory function by its $k = 0$ limit in the calculation of the dielectric friction, $\hat{\zeta}_{DF}(z)$. This method has been used rather successfully in explaining both the experimental and computer simulation results on solvation dynamics in a wide variety of systems (Bagchi and Roy 1993, Roy and Bagchi 1993a, b, Roy *et al.* 1993). It should be pointed out here that this procedure is entirely different from the continuum model method which also relates the single-particle memory function (the dielectric friction) to the dielectric function. We shall show that while the former breaks down completely in dipolar system, our microscopic procedure works quite well.

The main objective here is to develop a self-consistent microscopic description of orientational relaxation in slow dipolar liquids. This, however, requires one to address several connected issues which arise naturally. Therefore, we discuss the following specific subjects. First, a derivation of the expression for the collective memory function in the overdamped but non-Markovian limit is presented. A microscopic expression for the dielectric friction is also derived. Next, these expressions and also the continuum model predictions are verified via a Brownian dynamics simulation of a dipolar lattice. The single-particle friction is calculated by using the collective memory function. This finally allows one to calculate the single-particle orientational correlation function.

The results of this study are rather interesting. First, we find that the continuum model gives an erroneous frequency dependence of the dielectric friction obtained by computer simulation. Thus, this method of finding the memory functions is to be discarded. The microscopic method, on the other hand, provides a much better description of the dielectric friction. We have obtained the single-particle orientational correlation function directly from the collective memory function. The calculated single-particle dielectric friction by using this memory function exhibits a qualitatively correct frequency dependence and is quite different from $\Gamma_c(z)$. We discuss the reason for this difference.

This section has been split up into three subsections: subsection 5·1. Contains the theoretical formulations and the molecular hydrodynamic equations, while subsections 5·2. and 5·3. Contain the calculations of collective dissipative kernal and the single-particle friction, respectively.

### 5.1. *Theoretical formulation: the molecular hydrodynamic equations*

In this section, let us briefly summarize the essential features of the molecular hydrodynamic description of the orientational relaxation of a tagged particle in a dense dipolar liquid. The starting point is, as usual, a set of conservation equations of the relevant dynamical variables associated with the motion of the particle such as the position ($\mathbf{r}$), orientation ($\boldsymbol{\Omega}$) and time ($t$) dependent number density, $\rho_s(\mathbf{r}, \boldsymbol{\Omega}, t)$ and the spatial and angular momentum densities, $\mathbf{g}_T^s(\mathbf{r}, \boldsymbol{\Omega}, t)$ and $\mathbf{g}_R^s(\mathbf{r}, \boldsymbol{\Omega}, t)$, respectively. The relaxations of the momentum densities depend on the force field exerted by the time dependent fluctuations in the number density of the surrounding solvent molecules. This force field, acting on the tagged particle at position ($\mathbf{r}$) and orientation ($\boldsymbol{\Omega}$), can be derived from the density functional theory which gives the following general expression for the time dependent free energy functional of an inhomogeneous system (Bagchi and Chandra 1991)

$$\beta\mathscr{F}[\rho(t)] = \int \mathrm{d}\mathbf{r}\,\mathrm{d}\boldsymbol{\Omega}\,[\ln \rho_s(\mathbf{r},\boldsymbol{\Omega},t) - 1] + \int \mathrm{d}\mathbf{r}\,\mathrm{d}\boldsymbol{\Omega}\,[\ln \rho_0(\mathbf{r},\boldsymbol{\Omega},t) - 1]$$
$$- \int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\mathrm{d}\boldsymbol{\Omega}\,\mathrm{d}\boldsymbol{\Omega}'\, c_{s0}(\mathbf{r},\mathbf{r}',\boldsymbol{\Omega},\boldsymbol{\Omega}')\delta\rho_s(\mathbf{r},\boldsymbol{\Omega},t)\delta\rho_0(\mathbf{r}',\boldsymbol{\Omega}',t)$$
$$- \frac{1}{2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\mathrm{d}\boldsymbol{\Omega}\,\mathrm{d}\boldsymbol{\Omega}'\, c(\mathbf{r},\mathbf{r}',\boldsymbol{\Omega},\boldsymbol{\Omega}')\delta\rho_0(\mathbf{r},\boldsymbol{\Omega},t)\delta\rho_0(\mathbf{r}',\boldsymbol{\Omega}',t), \tag{37}$$

where $\delta\rho_0(\mathbf{r},\boldsymbol{\Omega},t) = \rho_0(\mathbf{r},\boldsymbol{\Omega},t) - \rho_0/4\pi$, is the fluctuation in the position and orientation dependent number density, $\rho_0(\mathbf{r},\boldsymbol{\Omega},t)$, of the solvent molecules and $\rho_0$ is the corresponding average number density. While $c_{s0}(\mathbf{r},\mathbf{r}',\boldsymbol{\Omega},\boldsymbol{\Omega}')$ represents the two-particle direct correlation function of the tagged particle and a solvent molecule, $c(\mathbf{r},\mathbf{r}',\boldsymbol{\Omega},\boldsymbol{\Omega}')$ corresponds to the direct correlation function between the two solvent molecules. These direct correlation functions are essentially the second-order expansion coefficients in the expansion of the free energy functional in the respective densities. The basic conservation equations for the motion of a tagged particle of mass $m_s$ and an average moment of inertia, $I_s$ may then be written as

$$\frac{\partial\rho_s(\mathbf{r},\boldsymbol{\Omega},t)}{\partial t} + \frac{1}{I_s}\nabla_\Omega\cdot\mathbf{g}^s_R(\mathbf{r},\boldsymbol{\Omega},t) + \frac{1}{m_s}\nabla_T\cdot\mathbf{g}^s_T(\mathbf{r},\boldsymbol{\Omega},t) = 0, \tag{38}$$

$$\frac{\partial\mathbf{g}^s_i(\mathbf{r},\boldsymbol{\Omega},t)}{\partial t} = -\rho_s(\mathbf{r},\boldsymbol{\Omega},t)\nabla_i\frac{\delta\mathscr{F}[\rho(t)]}{\delta\rho_s(\mathbf{r},\boldsymbol{\Omega},t)}$$
$$- \int_0^t \mathrm{d}t' \int \mathrm{d}\mathbf{r}'\,\mathrm{d}\boldsymbol{\Omega}'\,\Gamma_i(\mathbf{r},\mathbf{r}',\boldsymbol{\Omega},\boldsymbol{\Omega}',t,t')\mathbf{g}^s_i(\mathbf{r}',\boldsymbol{\Omega}',t')$$
$$+ \mathbf{F}_i(\mathbf{r},\boldsymbol{\Omega},t), \tag{39}$$

where $i = R, T$. $\nabla_T$ and $\nabla_R$ are the spatial and angular momenta operators, respectively. $\mathbf{F}_i(\mathbf{r},\boldsymbol{\Omega},t)$ represent the random force $\mathbf{F}(\mathbf{r},\boldsymbol{\Omega},t)$ and the random torque, $\mathbf{N}(\mathbf{r},\boldsymbol{\Omega},t)$ acting on the particle at position $\mathbf{r}$ and orientation $\boldsymbol{\Omega}$ at time $t$. In the relaxation of the spatial and angular momentum densities, the dissipative dynamics is determined by the corresponding memory kernels represented as $\Gamma_T(\mathbf{r},\mathbf{r}',\boldsymbol{\Omega},\boldsymbol{\Omega}',t,t')$ and $\Gamma_R(\mathbf{r},\mathbf{r}',\boldsymbol{\Omega},\boldsymbol{\Omega}',t,t')$, respectively. These are related to the force–force torque–torque autocorrelation functions respectively by the second fluctuation–dissipation theorem as

$$\Gamma_T(\mathbf{r},\mathbf{r}',\boldsymbol{\Omega},\boldsymbol{\Omega}',z) = \frac{\beta}{3}\int_0^\infty \mathrm{d}t\exp(-zt)\langle\mathbf{F}(\mathbf{r},\boldsymbol{\Omega},t=0)\cdot\mathbf{F}(\mathbf{r}',\boldsymbol{\Omega}',t)\rangle, \tag{40}$$

$$\Gamma_R(\mathbf{r},\mathbf{r}',\boldsymbol{\Omega},\boldsymbol{\Omega}',z) = \frac{\beta}{2}\int_0^\infty \mathrm{d}t\exp(-zt)\langle\mathbf{N}(\mathbf{r},\boldsymbol{\Omega},t=0)\cdot\mathbf{N}(\mathbf{r}',\boldsymbol{\Omega}',t)\rangle. \tag{41}$$

The solvent molecule may also be described using an identical set of conservation equations for the dynamical evolution of the solvent number density, $\rho_0(\mathbf{r},\boldsymbol{\Omega},t)$. Evidently, to solve these equations, the primary requisites are the static correlations as well as the dissipative kernels. The direct correlation functions may be obtained analytically using the MSA (Wertheim 1971, Gray and Gubbins 1984) model for systems having low polarity or can be estimated semi-analytically using theories like linearized hypernetted chain (LHNC) approximation (Gray and Gubbins 1984) for more polar systems. Clearly, it is the determination of the dissipative kernels that constitutes the most crucial step in deriving the single-particle orientational relaxation. The standard assumption made in the evaluation of the memory kernal is that the tagged particle is immobile; that is $\mathbf{r} = \mathbf{r}'$ and $\boldsymbol{\Omega} = \boldsymbol{\Omega}'$ in equations (40) and (41).

As mentioned earlier, the calculation of the dissipative kernel in the complex molecular liquids is extremely difficult and has not been achieved yet. In the absence of a consistent description of the full position and orientation dependence of the memory kernel, it may be assumed to be *local* in space and orientation, but *non-local* in time using the following condition

$$\Gamma_R(\mathbf{r}, \mathbf{r}', \boldsymbol{\Omega}, \boldsymbol{\Omega}', t, t') = \zeta(t - t')\delta(\mathbf{r} - \mathbf{r}')\delta(\boldsymbol{\Omega} - \boldsymbol{\Omega}'), \tag{42}$$

whereas $\zeta(t)$ is the rotational friction acting on the single particle. Note that this is the friction which is required to determine the single-particle orientational relaxation, using equations (6) and (7). But this assumption of the locality in space and orientation is not correct for treating the collective motion such as the collective orientational relaxation of the solvent molecules (as described by $C_{lm}(\mathbf{k}, t)$). In fact, the assumption of the locality in space can be easily removed and the resultant memory function can consequently be written as $\Gamma_R(\mathbf{r} - \mathbf{r}', t - t')$ in an isotropic medium. But the retention of the orientation dependence of the memory kernel is not simple and this would introduce a non-trivial rank dependence in the kernel. This has already been discussed at length in previous sections. Therefore, in the description of the collective orientational relaxation, we shall still use $\Gamma_R(\mathbf{k}, z)$ as an effective representation of the collective memory kernel.

### 5.2. *Calculation of the collective dissipative kernel by an inversion procedure*

The above set of hydrodynamic equations are solved most easily if one works in the Fourier space with the wave-vector $\mathbf{k}$ conjugate to the position vector $\mathbf{r}$ and also in the Laplace plane with $z$ as the Laplace frequency. Let us first present the solution of the above set of equations for the *pure solvent*. First, the fluctuating number density $\delta\rho_0(\mathbf{r}, \boldsymbol{\Omega}, t)$ is expanded in spherical harmonics

$$\delta\rho_0(\mathbf{k}, \boldsymbol{\Omega}, t) = \sum_{lm} a_{lm}(\mathbf{k}, t) Y_{lm}(\boldsymbol{\Omega}), \tag{43}$$

where $a_{lm}(\mathbf{k}, t) = \int d\boldsymbol{\Omega}\, Y^*_{lm}(\boldsymbol{\Omega})\delta\rho_0(\mathbf{r}, \boldsymbol{\Omega}, t)$. The direct correlation function can also be expanded in terms of the spherical harmonics

$$c(\mathbf{k}, \boldsymbol{\Omega}, \boldsymbol{\Omega}') = \sum_{l_1 l_2 m_1} c(l_1 l_2 m_1; \mathbf{k}) Y_{l_1 m_1}(\boldsymbol{\Omega}) Y_{l_2 m_1}(\boldsymbol{\Omega}'), \tag{44}$$

where $\mathbf{k}$ is chosen to be parallel to the $z$-axis. Then, the above molecular hydrodynamic theory gives the following expression for $a_{lm}(\mathbf{k}, z)$

$$a_{lm}(\mathbf{k}, z) = \frac{a_{lm}(\mathbf{k}, t = 0)}{z + \sum_{lm}(\mathbf{k}, z)}, \tag{45}$$

where $\Sigma_{lm}(\mathbf{k}, z)$ is the generalized rate of density relaxation and is given by (Roy and Bagchi 1993)

$$\sum\nolimits_{lm}(\mathbf{k}, z) = \frac{l(l+1)k_B T f(llm; k)}{I\Gamma_R(\mathbf{k}, z)} + \frac{k^2 k_B T f(llm; k)}{M\Gamma_T(\mathbf{k}, z)}, \tag{46}$$

where $M$ and $I$ are the mass and the average moment of inertia of a solvent molecule.

Note that both the memory kernels have been assumed to be non-local in space and time. In the subsequent discussion, we shall assume that $\Gamma_R(\mathbf{k}, z) = I\Gamma_R(\mathbf{k}, z)$ and $\Gamma_T(\mathbf{k}, z) = M\Gamma_T(\mathbf{k}, z)$. An important quantity which appears in the above expression is the orientational caging parameter, $f_{llm}(\mathbf{k}) = 1 - (\rho_0/4\pi)c(llm; \mathbf{k})$. In the limit of the single-particle dynamics (that is, $\mathbf{k} \to \infty$), $f_{llm}(\mathbf{k}) = 1$ but it plays a non-trivial role in the collective density relaxation. By using the linear response theory (Madden and Kivelson 1984, Chandra and Bagchi 1989, Bagchi and Chandra 1991), the above equation for the solvent density relaxation can be extended to obtain the following expression for the wave-vector and the frequency dependent longitudinal dielectric function, $\epsilon_L(\mathbf{k}, z)$ (Bagchi and Roy 1993, Roy and Bagchi 1993)

$$1 - \frac{1}{\epsilon_L(\mathbf{k}, z)} = \left[1 - \frac{1}{\epsilon_L(\mathbf{k})}\right]\left[1 - \frac{z}{z + \sum_{10}(\mathbf{k}, z)}\right]. \tag{47}$$

From the above discussion, it is evident that both the rotational and the translational dissipative kernels are required to evaluate the dynamical evolution of $a_{lm}(\mathbf{k}, z)$. The translation kernel, $\Gamma_T(\mathbf{k}, z)$ can be obtained directly from the dynamic structure factor using the following expression

$$\frac{k_B T}{\Gamma_T(\mathbf{k}, z)} = \frac{S(\mathbf{k})[S(\mathbf{k}) - zS(\mathbf{k}, z)]}{k^2 S(\mathbf{k}, z)}, \tag{48}$$

where $S(\mathbf{k})$ is the static structure factor. However, the determination of the full wave-vector and the frequency dependence of the rotational kernel is much more non-trivial and is not known yet. We next describe the inversion procedure adopted to determine this quantity from experiments.

If it is assumed that the wave-vector and frequency dependent rotational kernel, $\Gamma_R(\mathbf{k}, z)$, can be approximated by its $\mathbf{k} = 0$ limiting value, then the dissipative kernel can be obtained directly from experiments which measure the macroscopic (that is, $\mathbf{k} \to 0$) polarization relaxation, such as the dielectric relaxation. This, similar to equation (48), is an inversion technique where a fundamental microscopic quantity is derived from an experimentally measurable property of the system. The inversion of equation (47) yields the following relation between the rotational dissipative kernel, $\gamma_R(\mathbf{k}, z)$ and the frequency ($z$) dependent dielectric function, $\epsilon(z)$ in the *overdamped limit of angular momentum relaxation* (Roy and Bagchi 1993a, Komath and Bagchi 1993)

$$\Gamma_R^c(z) = \frac{2f(110; \mathbf{k} = 0)k_B T[\epsilon_0 - \epsilon(z)]}{z\epsilon_0[\epsilon(z) - 1]}. \tag{49}$$

Note that all the quantities appearing on the right-hand side of the above equation may be obtained from known experimental results. In particular,

$$f(110, \mathbf{k} = 0) = 3Y/(1 - 1/\epsilon_0),$$

where $3Y = (4\pi/3)\beta\mu^2\rho_0$ represents the polarity parameter of the solvent with dipole moment $\mu$. $\beta = (k_B T)^{-1}$.

### 5.3. *Calculation of the single particle friction, $\hat{\zeta}_R(z)$*

It has already been discussed in the previous section that for dipolar liquids, the single-particle friction, $\hat{\zeta}_R(z)$ may be resolved into a short-range part, denoted by $\zeta_0$ and also a dipolar part, termed usually as the dielectric friction, $\hat{\zeta}_{DF}(z)$. In the absence of any significant viscoelastic effects in the solvent, $\zeta_0$ is independent of frequency and can be obtained using the Stokes–Einstein relation. Therefore, calculation of the friction would evidently require the calculation of the dielectric friction from the torque–torque correlation function. The above formulation leads to the following microscopic expression of the torque

$$\mathbf{N}(\mathbf{r},\Omega,t) = -\rho_s(\mathbf{r},\Omega,t)\nabla_R \int \mathrm{d}\mathbf{r}'\,\mathrm{d}\Omega'\,c_{s0}(\mathbf{r},\mathbf{r}',\Omega,\Omega')\delta\rho_0(\mathbf{r}',\Omega',t'). \tag{50}$$

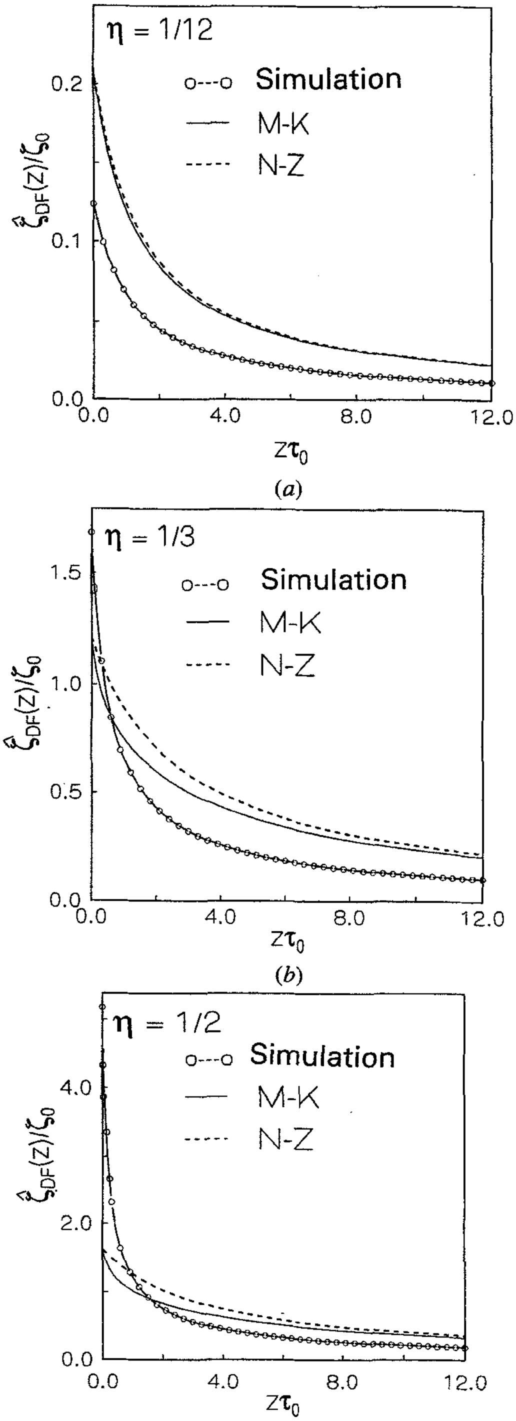
From this torque, one can indeed calculate the friction by using the well-known Kirkwood's formula (Boon and Yip 1980, Wolyes 1988), but this leads to a complex four-dimensional integration over the torque–torque autocorrelation function. Here we shall simplify the calculation of the friction by assuming that the tagged particle is immobile. This leads, after some tedious algebra, to the following expression for the dielectric friction

$$\beta\zeta_{DF}(z) = \frac{\rho_0}{2(2\pi)^4}\int_0^\infty \mathrm{d}k\,\mathbf{k}^2\left[\frac{c_{s0}^2(110;\mathbf{k})[1+(\rho_0/4\pi)h(110;\mathbf{k})]}{z+\Sigma_{10}(\mathbf{k},z)} + 2\,\frac{c_{s0}^2(111;\mathbf{k})[1-(\rho_0/4\pi)h(111;\mathbf{k})]}{z+\Sigma_{11}(\mathbf{k},z)}\right], \tag{51}$$

where $c(llm;\mathbf{k})$ and $h(llm;\mathbf{k})$ are the $(llm)$ components of the direct correlation function and the pair correlation function in the intermolecular frame with $\mathbf{k}$ parallel to the $z$-axis (Bagchi and Chandra 1991). In deriving the above expression, we have assumed that the intermolecular correlations are given by a linear theory (such as MSA or LHNC) (Wetheim 1971, Gray and Gubbins 1984). so that the only non-vanishing components of the direct correlation function are $c(000;\mathbf{k})$, $c(110;\mathbf{k})$ and $c(111;\mathbf{k})$. As already mentioned, we have used the collective (that is, $\mathbf{k}=0$) approximation for the rotational dissipative kernel. This expression for dielectric friction will now be used in the generalized diffusion equation to obtain the single particle orientational correlation function.

Equation (51) has an interesting structure. It shows that the dielectric friction can be sensitive to the local orientational correlations. Moreover, both the longitudinal and the transverse modes contribute to the dielectric friction. Note that by the transverse mode, we mean here the (111) component in the coordinate frame when $\mathbf{k}$ is along the $z$-axis-these are *not* the transverse electromagnetic modes. Lastly, in the Markovian limit, equation (51) reduces exactly to the expressions of Nee and Zwanzig (N–Z) (1970) and of Hubbard and Wolynes (1970) if the *both the local correlations and the effects of the translational modes are neglected* (Bagchi and Vijayadamodar 1993). We shall soon discuss the predictions of equation (51).

As already mentioned, one of the objectives of the present discussion is to understand the nature of memory functions that are involved in the single-particle and collective orientational relaxation. Towards this goal, the results of the available memory functions are compared with the Brownian dynamics simulations discussed previously in section 2. In figure 11 the simulated frequency dependent single-particle dielectric friction is plotted for three different polarities and compared with the predictions of N–Z and M–K theories. As can be seen from the figure 11 (*a*, *b* and *c*) both the theories fail to capture much of the observed behaviour, although the M–K



(*a*)

(*b*)

(*c*)

Figure 11. Simulated frequency dependence of single-particle dielectric friction is compared with the predictions of Nee–Zwanzig (N–Z) and Madden–Kivelson (M–K) at three different polarities at (*a*) $\eta = 1/12$, (*b*) $\eta = 1/3$, (*c*) $\eta = 1/2$. The frequency is scaled by $\tau_0$, where $\tau_0 = (2D_R)^{-1}$.

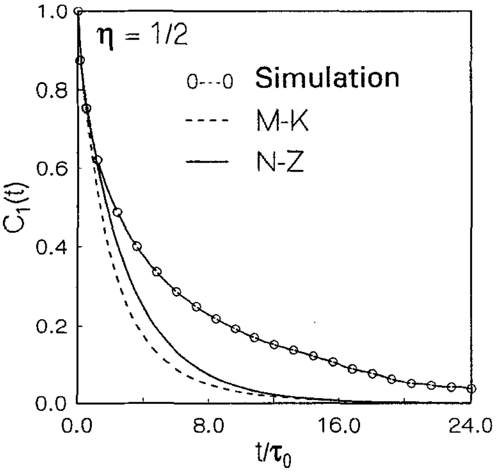


Figure 12. Comparison of simulated single-particle orientational correlation function ($C_1(t)$) with the theories of Nee–Zwanzig (N–Z) and Madden–Kivelson (M–K) at $\eta = 1/2$. Time is scaled by $\tau_0$.

theory does a slightly better job than that of N–Z. Note that this particular model simulation satisfies all the assumptions that are usually made in continuum mode calculations. Therefore, the breakdown of the continuum model can only be attributed to the neglect of the local intermolecular orientational correlations—the long-range correlations are, or course, correctly included in the continuum model theory. The failure of M–K theory is perhaps due to the use of the asymptotic form of the orientational pair correlation function, although the basic formalism of this theory is rigorous and almost identical to the one described here in the last section.

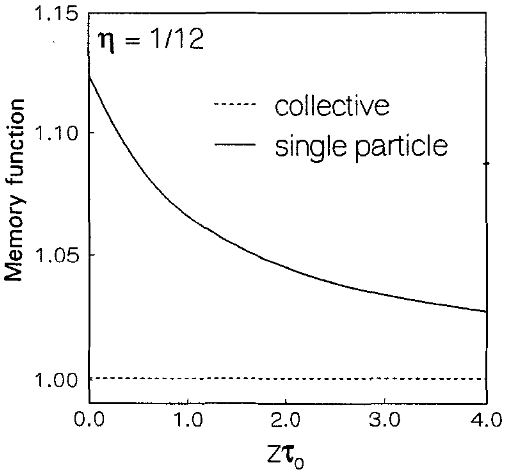
In figure 12, the time dependence of the simulated single-particle correlation function has been compared with the predictions of the N–Z and M–K theories. The theories predict much faster decay which can be seen from figure 12 (*c*). Details of $C_1(t)$ are available elsewhere (Zhou and Bagchi 1992, Zhou *et al.* 1992, Ravichandran and Bagchi 1994a, c).

We now turn out attention to the comparison between the single-particle and collective memory functions, $\hat{\zeta}_R(z)$ and $\Gamma_c(z)$, respectively. The collective memory functions obtained *exactly* from equation (49) of the last section, except the quantity $f_L(\mathbf{k} = 0) = (s + 8\pi/3)$, where the values of ($s$) for three different polarities ($\eta$ = (1/12), (1/3), (1/2)) are 13·15, 5·88, 5·45. (Zhou 1993b) respectively. Note that both the above quantities are obtained from computer simulations (Zhou 1993b). The frequency dependence of these functions are depicted in figure 13 (*a*, *b*, *c*). As can be seen from the figures, *these two functions have entirely different frequency dependencies*. The collective memory function exhibits much weaker frequency dependence. This is because the frequency dependent dielectric functions are only weakly non-Debye even at the highest polarity that could be considered here—the situation changes drastically when $\epsilon(z)$ is strongly non-Debye, as will be discussed in the next section.

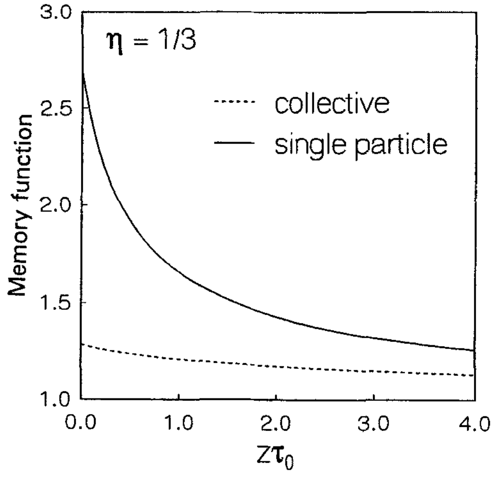
Next, the prediction of the microscopic equation (51) are compared with the simulations of the Brownian dipolar lattice. In figure 14 we present this comparison for the frequency dependence of $\hat{\zeta}_{DF}(z)$— it is clear that the agreement is much better than what has been obtained from the continuum models or the Madden–Kivelson theory. In figure 14 the calculated $C_1(t)$ (obtained by using the calculated $\hat{\zeta}_{DF}(z)$ in the generalized diffusion equation) is compared with the simulations—again the agreement is quite satisfactory, especially when compared with the other theories.

The solid line in figure 14 has been generated completely from first principles—no adjustable parameter has been used. The agreement seem to indicate that the basic postulates of the molecular hydrodynamic theory are reasonably valid. As discussed earlier, equation (51) reduced to the continuum limit result when the appropriate limits are taken (Bagchi and Vijayadamodar 1993). The main difference between equation (51) and the continuum models is that the former includes the effects of the local intermolecular orientational correlations. The latter are important in enhancing the magnitude of dielectric friction, especially at small frequencies, that is, in the long time, better than the other theories.

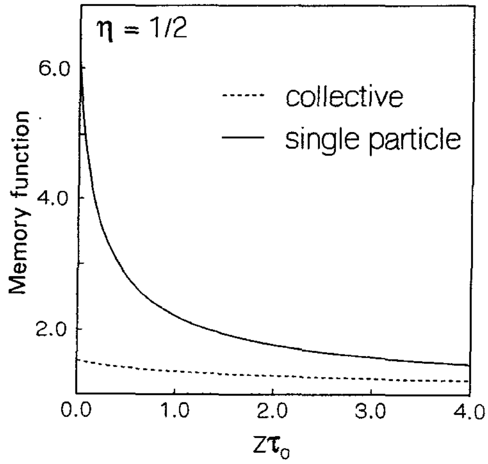
Note that in the recently developed theories of solvation dynamics, two rather different expression of memory functions have been used. In the solvation dynamics the memory function that enters naturally is the wave-vector and frequency dependent



(*a*)



(*b*)



(*c*)

Figure 13. Simulated frequency dependence of single particle friction is compared with the collective ($\mathbf{k} = 0$ limit) memory function at (*a*) $\eta = 1/12$, (*b*) $\eta = 1/3$, (*c*) $\eta = 1/2$. The collective memory function is obtained by using the simulated dielectric function, $\epsilon(z)$. The frequency is scaled by $\tau_0$. Note that the single-particle friction is $\zeta_0 + \zeta_{DF}$.

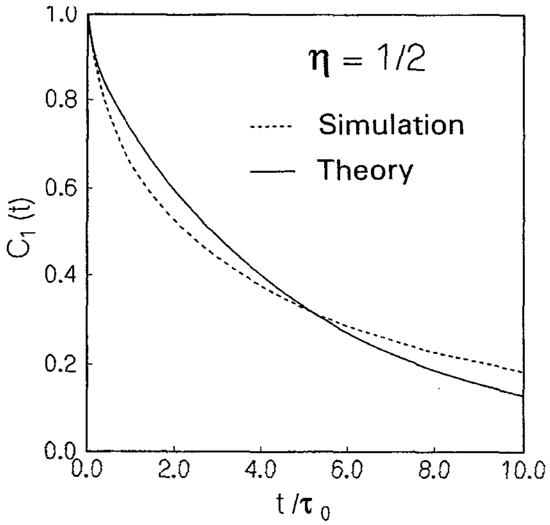


Figure 14. The comparison of single-particle orientational correlation function, $C_1(t)$ in a Brownian dipolar lattice calculated by using equation (51) with that obtained from simulations at $\eta = 1/2$. As in figure 13, the collective memory function is obtained using the simulated dielectric function, $\epsilon(z)$. The time is scaled by $\tau_0$.

quantity $\Gamma_R(\mathbf{k}, z)$, which has been introduced in the last section. The long wavelength limit of this wavefunction is the collective memory function $\Gamma_c(z)$, while at the small wavelength $\Gamma_R(\mathbf{k}, z)$ reduces to the single-particle friction. In the initial theory of Chandra and Bagchi (Bagchi 1989, Chandra and Bagchi 1989) the single-particle friction ($\hat{\zeta}_R(z)$) was used in place of $\Gamma_R(\mathbf{k}, z)$, while in the later the collective memory function was used (Bagchi and Roy 1993, Roy and Bagchi 1993a, Roy *et al.* 1993). The present study indicates that it might be necessary to include the full wave-vector dependent $\Gamma_R(\mathbf{k}, z)$, if, a description that is reliable both at short and long times is required. However, for solvation dynamics of an ion the collective approximation for the memory function should be more reliable, especially at short times, than the single-particle approximation. This is because the short time solvation dynamics of an ion is dominated by the long wavelength polarization response (Bagchi and Roy 1993, Roy and Bagchi 1993). Recently Zhou (1993) has shown that one can successfully explain the time dependence of the single-particle correlation function in Brownian dipolar lattice by using the collective memory function in a scheme similar to the present one. This also justified the validity of the method of translation of the information from experiments to the memory function, as proposed here.

The above discussions considered only the immobile solute for calculating the memory function. Some calculations allowing for the mobility have also been studied. These calculations show that of $\zeta(t)$ is found to decay much faster in the mobile solute than in that of immobile case. This kind of observation has also been observed by Papazyan and Maroncelli (1994).

Before we end this section, a brief mention must be made of several related, highly interesting work. Alavi and Waldeck, (1991, 1993, 1994) have removed the point dipole approximation of the usual continuum models by employing a realistic discrete charge distribution and obtained generalized expression for the rotational dielectric friction. For the organic dye molecules that were commonly used for studies of orientational relaxation, the results of Alavi and Waldeck (1994) appear to be in better agreement with the known experimental results than the simple continuum models. In some cases, however, the discrete charge distribution model leads to too large a value of the dielectric friction. This seems to reflect an inherent limitation of the continuum model. When a charge is placed close to the surface of a molecule (which is still assumed to be inside a cavity), then the polarizaton of the liquid is very large because the distance of the charge from the dielectric continuum is small. This leads to a very large fluctuating force and hence a large friction. This unphysical prediction is due to the neglect of the molecularity of the dipolar liquid in the continuum modes. In a real liquid, the closest distance of approach between any two molecules is bounded from below by the sum of the radii of the molecules. In the continuum model, this distance can approach zero if the charge is in the surface of the solute molecular cavity because the solvent is assumed to be a structureless continuum. A microscopic study of this effect, will be worthwhile.

In very recent work Papazyan and Maroncelli (1994) presented a very detailed study of the rotational dielectric friction in the same Brownian dipolar lattice discussed earlier. There are several new features of this study. These authors considered the rotational relaxation of a dipolar solute different from the solvent molecules. They also studied the rank dependence of the dielectric friction, with results almost identical to the ones obtained earlier by us (Ravichandran and Bagchi 1994a). Another important finding is that the dielectric friction experienced by the solute dipole is substantially smaller if the solute is allowed to move rather than keeping it fixed, as assumed in most theories.

They also find that the time dependence of $E$-field correlation functions match that of $\hat{\zeta}_R(t)$ reasonably well in the immobile case but are much too fast in the mobile solute case. They also find that the discrepancy becomes worse when intrinsic rotation time is faster than that of the solvent. So, in all the cases reported above we have used only fixed solute to get the dielectric friction. However, the physical significance of the friction on a moving solute is not very clear at this point. The detailed study of Papazyan and Maroncelli will certainly serve as a reference point for future developments in this area.

## 6. Orientational caging of translational motion

In dense molecular liquids at low temperatures, the dynamics is determined largely by the short-range order that is present in the system. This short-range order essentially means the arrangement and packing of the molecules in space. This packing is, in turn, determined by the nature of the intermolecular interactions. In contrast to atomic liquids, where only spherical interactions are involved, angle dependent interactions often dominate the total potential energy in molecular liquids. This gets reflected in the local molecular arrangements. This molecular arrangement can be represented in terms of distance and angle dependent radial distribution functions, $g(\mathbf{r}_1 - \mathbf{r}_2, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2)$, which describes correlation between two molecules with coordinates $(\mathbf{r}1, \boldsymbol{\Omega}_1)$ and $(\mathbf{r}2, \boldsymbol{\Omega}_2)$. At low temperatures, there can be significant degree or orientational correlations among the molecules. The importance of these correlations on the dynamical properties of molecular liquids is not well-understood yet, except perhaps for liquid crystals. However, *the orientationally correlated molecules figured many times in the qualitative* discussions on slow relaxation in molecular liquid, most notably in the discussions of Frenkel (1955, 1989). We should point out that the orientational pair correlations being discussed here is different from the bond orientational order discussed extensively in the recent past (Dattagupta and Turski, 1985, 1993, Dattagupta, 1994).

Now, the effects of spatial correlations on slowing down of spatial density relaxation is known for a long time (Boon and Yip 1980, Wolynes 1988). This caging is clearly manifested in the sharp first peak in the static structure factor. This caging plays an important role in the mode coupling theory of glass transition. There is another related effect which has been discussed earlier, that is, the 'hidden' role of translational motion in reducing the magnitude of rotational dielectric friction. There is, however, a forth aspect which is the role of orientational caging on the translational motion. To the best of our knowledge this aspect has not been discussed earlier by Ravichandran *et al.* (1994d). Therefore, we briefly describe this point. In dense molecular liquids, orientational motion will lead to a change in the force-field experienced by a molecule. Thus, orientational motion can contribute significantly to the frictional forces experienced by a molecule. In the below we briefly discuss some preliminary studies carried out of the effects of this orientational caging by our group—we are not aware of any other microscopic study.

A microscopic expression for the effects of orientational correlation on the friction can be obtained by using the molecular hydrodynamic theory described earlier. This theory provides a simple expression for the force acting on a tagged molecule,

$$\mathbf{F}(\mathbf{r}, \boldsymbol{\Omega}, t) = \nabla \int \mathrm{d}\mathbf{r}' \, \mathrm{d}\boldsymbol{\Omega}' \, c(\mathbf{r} - \mathbf{r}', \boldsymbol{\Omega}, \boldsymbol{\Omega}', t) \delta\rho_0(\mathbf{r}', \boldsymbol{\Omega}', t). \tag{52}$$

We can then use Kirkwood's formula (Boon and Yip 1980, Wolynes 1988) to find the friction on the tagged molecule. A somewhat lengthy calculation leads to the following expression for the translational friction

$$\hat{\zeta}_{\text{trans}}(z) = \frac{k_B T}{6\pi^2 \rho_0} \int_0^\infty d\mathbf{k}\mathbf{k}^4 \sum_{l_1 l_2 m} \frac{[(\rho_0/4\pi) c(l_1 l_2 m; \mathbf{k})]^2 S(l_1 l_2 m; \mathbf{k})}{z + \sum\limits_{l_1 l_2 m} (\mathbf{k}, z)}, \tag{53}$$

where $S(l_1 l_2 m; \mathbf{k})$ are the orientational structure factors, related to $c(l_1 l_2 m; \mathbf{k})$ by

$$S(l_1 l_2 m; \mathbf{k}) = [1 - (-1)^m c(l_1 l_2 m; \mathbf{k})]^{-1}. \tag{54}$$

In deriving the above expression, we have neglected the self-motion of the tagged molecule. Note that if we neglect orientational caging, then we obtain essentially the same expression obtained earlier by Sjogren and Sjolander (1979) where it comes from the ring term of the density fluctuations. Wolynes (1988) has discussed elsewhere the validity of this approach to treat dynamics of slow liquids.

The above equation shows that in slow liquids, orientational relaxation can contribute significantly to the translational friction. This is perhaps the first quantitative expression for the effects of orientational correlations on translational mobility.

A preliminary numerical calculation of the total translational friction has been carried out in order to estimate the magnitude of orientational caging, by using the orientational correlations for a dipolar hard sphere model. In table 4 we show the results of such a calculation are presented. In this calculation, a dipolar liquid at the reduced density $\rho_0\sigma^3 = 0{\cdot}8$ has been considered and the value of the dielectric constant has been varied. The integral in equation (53) was evaluated only under the Markovian approximation. The dynamic structure factor has been assumed to be given by $S(\mathbf{k}, t) = S(\mathbf{k}) \exp(-D_{T0} k^2 t / S(\mathbf{k})]$, where $D_{T0}$ is the bare self diffusion coefficient related to the bare translational friction $\zeta_{T0}$ by $D_{T0} = k_B T/\zeta_{T0}$. The above representation of $S(\mathbf{k}, t)$ is expected to be reliable at intermediate to large $\mathbf{k}$ values. In table 4, the contributions of the isotropic term ($\zeta_{TT}$) and the angular term ($\zeta_{TR}$) are shown separately. Because we have used the correlation functions from MSA, the isotropic part is invariant to the variation of the dielectric constant of the medium. It can be seen from the values that effects of the orientational caging of translational motion are clearly significant. Based on this calculation, we anticipate that they may be cases where orientational contribution to the translational friction can be comparable to the usually considered isotropic part. This can have important consequences and certainly deserves further study.

Table 4. The relative contributions of the rotational part ($\zeta_{TR}$) and the translational part ($\zeta_{TT}$) to the total translational friction ($\zeta_T = \zeta_{TT} + \zeta_{TR}$) calculated from equation (53), for a dipolar liquid of density $\rho\sigma^3 = 0{\cdot}8$ ($\sigma$ = molecular diameter) and the ratio $D_{T0}/2D_{R0}\sigma^2$ where $D_{i0}(i = T, R)$ are the bare diffusion constants.

| $\epsilon_0$ | $\zeta_{TT}/\zeta_{T0}$ | ${}_{TR}/\zeta_{T0}$ |
|---|---|---|
| 10 | 2·18 | 0·21 |
| 20 | 2·18 | 0·40 |
| 33 | 2·18 | 0·59 |
| 50 | 2·18 | 0·81 |

## 7. Conclusions

Orientational relaxation of a tagged molecule in a dense molecular liquid is a complicated process. Not only does the orientational motion derive contributions from many different kinds of molecular motions, but the relative weights of these contributions are again complex functions of molecular arrangements. The situation is further complicated for dipolar liquids where the long range and anisotropic nature of dipolar interactions introduce non-trivial static and dynamic correlations that need to treated consistently. So long one is happy with the continuum-hydrodynamic description, these complications do not raise their ugly head; but as soon as a microscopic description is attempted, the enormity of the problem becomes obvious.

In such a situation, the theoretical studies have been naturally devoted to the simplest molecular models—dipolar lattice, polar hard spheres and Stockmayer liquids. Still, the progress has been rather slow. An appropriate example of the difficulty is provided by the calculation of the dielectric friction. Even when it is approximated by the Kirkwood's formula for friction on a fixed dipole, the mean-field calculation cannot be carried out rigorously because no accurate expression for the wave-vector and frequency dependent memory function $\Gamma_R(\mathbf{k}, z)$, is yet available. When the collective memory function is approximated by the single-particle value (that is, the $\mathbf{k} \rightarrow \infty$ limit of $\Gamma_R(\mathbf{k}, z)$), then too small an effect of dipolar interactions is predicted. In the opposite limit, the replacement of $\Gamma_R(\mathbf{k}, z)$ by its $\Gamma_R(\mathbf{k} = 0, z)$ limit leads to a much better effect—but the justification of this approximation is unclear.

In this review, we have focused on the collective effects in the single-particle orientational relaxation. Since, this problem is intimately connected with the problem of collective orientational relaxation, a brief review of the same has also been provided. A big boost to the whole field of relaxation in dipolar liquids has come recently from solvation dynamics. Therefore, a brief review of the latter is also provided to make the review self-contained.

The main theme of the present review is that all the (seemingly) different problems in the field of dynamics of dense dipolar liquids are strongly affected by the presence of intermolecular correlations in these liquids. Any microscopic theory must pay proper attention to these correlations. The situation is further complicated by the different dissipative mechanisms that are present in a dense dipolar liquid.

Finally we come back to the question asked in the title: how much do we really understand the role of correlations in the dynamics of dipolar liquids? In order to put the question in proper perspective, let us first recall that even a few years ago, the main theoretical framework available was the continuum model. Although it was realized by all and sundry that the continuum model is inadequate and should be discarded, the real thrust for doing so has come only now. The microscopic description that has been developed recently by us (Chandra and Bagchi 1991) and by others (Wei and Patey 1990, Raineri *et al.* 1992,), includes the correlations properly and appears to be more successful (than the continuum model) in describing the detailed dynamics. An example is the single-particle correlation function $C_1(t)$ of a Brownian dipolar lattice where the microscopic theory fares substantially better than the continuum models of Nee and Zwanzig and Hubbard and Wolynes. However, further advances has been plagued by the lack of the reliable equilibrium orientational correlations functions. Unfortunately, these functions have yet to be measured experimentally. Regarding the dissipative kernals (or the memory functions), some progress has been made but a detailed picture has yet to emerge. Thus, to answer the question on the extent of our understanding of the effects of intermolecular correlations on dynamics, our answer is that it is still rather poor. A lot more effort is needed in this field to obtain a satisfactory understanding. Given the importance of this field in chemistry, such an effort will certainly be worthwhile.

We end this review by discussing a few specific problems for future study. On the theoretical side, a quantitative description of the wave-vector and frequency dependent memory function is required. This is necessary to understand the observed significant difference between the memory functions for single-particle and the collective correlation function, as described in section 5. There is also the need to understand why the simulated memory function for the mobile solute fails to describe the single-particle orientational dynamics. Fortunately though, the microscopic description of $C_1(t)$ has been rather satisfactory. This may just indicate that in this particular case, the approximation of replacing the wave-vector and frequency dependent memory function by its long wavelength (that is, $\mathbf{k} = 0$) limit is not serious. However, this requires further verification. There is, of course, the need to understand polar effects on orientation of real molecules, especially of charged organic dye molecules which are often used as probes to test the theories. A step towards this goal has already been taken by Alavi and Waldeck (1991, 1993, 1994), who considered a realistic charge distribution, instead of treating them as a point charge or a point dipole at the centre of a sphere. A microscopic study of this problem will be worthwhile. A more ambitious project would be to consider protic liquids. Here a treatment similar to the one developed by Raineri, Friedman and coworkers (1992, 1993, 1994a, b) can be a useful starting point. On the computational side, there is the need to simulate at least a few more model systems, such a face centred dipole lattice. Another good candidate is the system of soft dipolar spheres. This system has been the focus of much study in recent years (Kusalik 1990, Wei and Patey 1992). However, the questions discussed here have not yet been asked. Another attractiveness of this system is that we can study in detail the role of the translational modes of the molecules—an aspect deliberately avoided in this review. On the experimental side, one would like to see systematic studies which aim primarily at understanding the effects of the polarity. Although, systematic studies of orientational relaxation exist for non-polar liquids (Ben-Amotz and Scott 1987), similar studies for dipolar liquids do not seem to exist. Thus, the field of orientational relaxation in dipolar systems still offers a large number of interesting problems which should keep the field active for many years to come.

## Acknowledgments

It is a pleasure to thank Professor Mark Maroncelli and Dr H.-X. Zhou for collaboration, help and discussions throughout the course of the study reported here. Thanks are also due to Ms Srabani Roy for collaboration in the work reported in sections 4 and 5 and for much help in preparing this manuscript. We are also grateful to Professor R. Zwanzig for discussions and comments in the early stage of the project. Helpful discussions with Dr S. Yashonath are gratefully acknowledged. We also thank Pinaki Mazumdar for helping in various stages. This work was supported in part by the Department of Science and Technology, India, the University Grants Commission (U.G.C.) and the Council of Scientific and Industrial Research (C.S.I.R.), India. We are grateful to the Supercomputer Education and Research Centre (S.E.R.C.) of Indian Institute of Science, Bangalore for computational facilities.

## References

ALAVI, D. S., and WALDECK, D. H., 1991, *J. chem. Phys.*, **94,** 6196; 1993, *Ibid.*, **98,** 3580; 1994, *Ultrafast Dynamics of Chemical Systems*, edited by J. D. Simon (Dordrecht: Kluwer).

ALLEN and TILDESLEY, 1987, *Computer Simulation of Liquids* (London: Clarendon).

ASCARELLI, G., 1976, *Chem. Phys. Lett.*, **39,** 23.

BAGCHI, B., 1989, *Ann. Rev. phys. Chem.*, **40,** 115; 1994, *J. chem. Phys.*, **100,** 6658.

BAGCHI, B., and CHANDRA, A., 1990, *Phys. Rev. Lett.*, **64,** 455; 1991, *Adv. chem. Phys.*, **80,** 1. (and references cited therein); 1992, *J. chem. Phys.*, **97,** 5126; 1993, *Chem. Phys.*, **173,** 133.

BAGCHI, B., CHANDRA, A., and RICE, S. A., 1990, *J. chem. Phys.*, **93,** 8991.

BAGCHI, B., and ROY, S., 1993, *Ultrafast Chemical Reactions and Solvent Effects*, edited by Y. Gauduel and P. J. Rossky (New York: American Institute of Physics), p. 269.

BAKSHIEV, N. G., 1964, *Opt. Spectrosc.*, **16,** 446.

BAKSHIEV, N. G., MAZURENKO, YU. T., and PITERSKAYA, I., 1966, *Opt. Spectrosc.*, **21,** 307.

BARBARA, P. F., and JARZEBA, W., 1990, *Adv. Photochem.*, **15,** 1.

BARBARA, P. F., WALKER, G. C., and SMITH, T. P., 1992, *Science*, **256,** 975.

BARTHEL, J., BACHHUBER, K., BUCHNER, R., GILL, J. B., and KLEEBAUER, M., 1990, *Chem. Phys. Lett.*, **167,** 62.

BARTHEL, J., BUCHNER, R., GILL, J. B., and KLEEBAUER, M., 1991, *Pure appl. Chem.*, **63,** 1473.

BEN-AMOTZ, D., and SCOTT, T. W., 1987, *J. chem. Phys.*, **87,** 8739.

BERNE, B. J., BOON, J. P., and RICE, S. A., 1966, *J. chem. Phys.*, **45,** 1086; 1967, *Ibid.*, **47,** 2283; 1986, *Ibid.*, **48,** 2833.

BERNE, B. J., and PECORA, R., 1976, *Dynamic Light Scattering* (New York: Wiley).

BOON, J. P.,. and YIP, S., 1980, *Molecular Hydrodynamics* (New York: McGraw-Hill).

BÖTTCHER, C. G. E., and BORDEWIJK, P., 1979, *Theory of Electric Polarization* (Amsterdam: Elsevier), Vol. II.

CALEF, D. F., and WOLYNES, P. G., 1983, *J. chem. Phys.*, **78,** 4145.

CARTER, E. A., and HYNES, J. T., *1991*, *J. chem. Phys.*, **94,** 5961.

CHAN, D. Y. C., MITCHELL, D. J., and NINHAM, B. W., 1979, *J. chem. Phys.*, **70,** 2946.

CHANDRA, A., and BAGCHI, B., 1989a, *J. chem. Phys.*, **90,** 1832; 1989b, *Ibid.*, **91,** 1829; 1989c, *Ibid.*, **91,** 3056; 1989d, *J. phys. Chem.*, **93,** 6996; 1990, *Physica* A, **169,** 246; 1991a, *Chem. Phys.*, **156,** 323; 1991b, *Proc. Indian Acad. Sci.*, (*Chem. Sci*) **103,** 77; 1993, *J. chem. Phys.*, **173,** 133.

CHO, M., DU, M., SCHERER, N. F., FLEMING, G. R., and MUKAMEL, S., 1993, *J. chem. Phys.*, **99,** 2410.

CHO, M., ROSENTHAL, S. J., SCHERE, N. F., ZEIGLER, L. D., and FLEMING, G. R., 1992, *J. chem. Phys.*, **96,** 5033.

COLE, R. H., 1989, *Ann. Rev. phys. Chem.*, **40,** 1.

DEBYE, P., 1929, *Polar Molecules* (New York: Dover).

DUTT, G. B., DORAISWAMY, S., and PERIASAMY, N., 1991, *J. chem. Phys.*, **94,** 5360.

DATTAGUPTA, S., and TURSKI, L. A., 1985, *Phys. Rev. Lett.*, **54,** 2359; 1993, *Phys. Rev.* E, **47,** 1222.

DATTAGUPTA, S., 1994, *J. non-crystalline Solids*, **172–174,** 197.

FATUZZO, E., and MASON, P. R., 1967, *Proc. phys. Soc.*, **90,** 729.

FINCHAM, D., 1981, *Daresbury Information Quarterly for MD and MC Simulations* (CCP5Q)., **2,** 6.

FIXMAN, M., and RIDER, K., 1969, *J. chem. Phys.*, **51,** 2425.

FLEMING, G. R., 1986, *Chemical Applications of Ultrafast Spectroscopy* (Oxford: Clarendon).

FLEMING, G. R., and WOLYNES, P. G., 1990, *Phys. Today.*, **43,** 36.

FONSECA, T., and LADANYI, B. M., 1991, *J. phys. chem.*, **95,** 2116.

FRENKEL, J., 1955, *Kinetic Theory of Liquids* (New York: Dover).

FRENKEL, D., 1989, *Simple Molecular Systems at Very High Density*, edited by A. Polian, P. Loubeyre and B. Boccara, NATO Series B: Physics Vol. 186 (New York: Plenum), p. 411.

FRIED, L. E.,. and MUKAMEL, S., 1990, *J. chem. Phys.*, **93,** 932.

FRÖHLICH, H., 1958, *Theory of Dielectrics* (Oxford: Clarendon Press).

GAUDUEL, Y., 1992, *J. molec. Liq.*,

GERSCHEL, A., 1984, *Molecular Liquids—Dynamics and Interactions*, edited by A. J. Barnes, W. J. Orville-Thomas, and J. Yarwood, (New York: Plenum), p. 163.

GÖTZE, W., and SJÖGREN, L., 1987, *J. Phys.*, C, **65,** 415.
GRAY, C. G., and GUBBINS, K. E., 1984, *Theory of Molecular Fluids* (Oxford: Clarendon), Vol. I.
GUILLOT, B., and BRAITOS, S., 1977, *Phys. Rev.* A, **16,** 424.
GUILLOT, B., MARTEAU, P., and OBRIOT, J., 1990, *J. chem. Phys.*, **93,** 6148.
HANSEN, J. P., and MCDONALD, I. R., 1986, *Theory of Simple Liquids* (London: Academic).
HASTED, J. B., HUSSAIN, S. K., FRESCURA, F. A. M., and BIRCH, J. R., 1985, *Chem. Phys. Lett.*, **118,** 622.
HUBBARD, J. B., and WOLYNES, P. G., 1978, *J. chem. Phys.*, **69,** 998.
HYNES, J. T., 1994, *Ultrafast Dynamics of Chemical Systems*, edited by J. D. Simon (Dordrecht: Kluwer).
KAWASAKI, K., 1994, *Phys. Rev.* A, (in press).
KIRKPATRICK, T. R., 1985, *Phys. Rev.* A, **31,** 939.
KIRKWOOD, J. G., 1936, *J. chem. Phys.*, **4,** 592.
KIVELSON, D., and KIVELSON, S. J., 1989, *J. chem. Phys.*, **90,** 4464.
KIVELSON, D., and MILES, D., 1988, *J. chem. Phys.*, **88,** 1925.
KOMATH, S. S., and BAGCHI, B., 1993, *J. chem. Phys.*, **98,** 8987.
KOSOWER, F. M., and HUPERT, D., 1986, *Ann. Rev. phys. Chem.*, **37,** 127.
KUSALIK, P. G., 1990, *J. chem. Phys.*, **93,** 3520.
LOBO, R., ROBINSON, J. E., and RODRIGUEZ, S., 1973, *J. chem. Phys.*, **59,** 5922.
LORING, R. F., and MUKAMEL, S. F., 1987, *J. chem. Phys.*, **87,** 1272.
LOTSHAW, W. T., and MCMORROW, D., 1991, *J. phys. Chem.*, **95,** 10395.
LYNDEN-BELL, R. M., 1984, *Molecular Liquids Dynamics and Interactions*, edited by A. J. Barnes, W. J. Orville-Thomas, and J. Yarwood (New York: Plenum), p. 501.
MADDEN, P., and KIVELSON, D., 1982, *J. phys. Chem.*, **86,** 4244; 1984, *Adv. chem. Phys.*, **56,** 467.
MARONCELLI, M., 1991, *J. chem. Phys.*, **94,** 2084; 1993, *J. molec. Liq.*, **57,** 1.
MARONCELLI, M., and FLEMING, G. R., 1988, *J. chem. Phys.*, **89,** 5044.
MARONCELLI, M., MACINNIS, J., and FLEMING, G. R., 1989, *Science*, **243,** 1674.
MARONCELLI, M., *et al.* 1994, *Ultra-Fast Chemical Reactions and Sòlvent Response*, edited by Y. Gauduel and P. J. Rossky (New York: AIP).
MAZURENKO, YU, T., and BAKSHIEV, N. G., 1970, *Opt. Spectrosc.*, **28,** 490.
MCCONNEL, J., 1991, *J. molec. Liq.*, **48,** 99.
MUNAKATA, T., 1978, *J. phys. Soc. Japan*, **45,** 749; 1985, *Prog. theor. Physics*, **73,** 570.
NEE, T.-W., and ZWANZIG, R., 1970, *J. chem. Phys.*, **52,** 6353.
NERIA, E., and NITZAN, A., 1992, *J. chem. Phys.*, **96,** 5433.
NERIA, N., NITZAN, A., BARNETT, R. N., and LANDMANN, U., 1991, *Phys. Rev. Lett.*, **67,** 1011.
NICHOLOSS III, A. L., and CALEF, D. F., 1988, *J. chem. Phys.*, **89,** 3783.
ONSAGER, L., 1993, *J. Am. chem. Soc.*, **58,** 1486.
PAPAZYAN, A., and MARONCELLI, M., 1991, *J. chem. Phys.*, **95,** 9219; 1994, *J. chem. Phys.* (submitted).
PAYNE, V. A., FORSYTH, M., KOLAFA, J., and RATNER, M. A., 1993, *J. phys. Chem.*, **97,** 10478.
PERERA, L., and BERKOWITZ, M. L., 1992, *J. chem. Phys.*, **97,** 5253.
RAINERI, F. O., RESAT, H., and FRIEDMAN, H. L., 1992, *J. chem. Phys.*, **96,** 3068.
RAINERI, F. O., RESAT, H., PERNG, B.-C., HIRATA, F., and FRIEDMAN, H. L., 1994a, *J. chem. Phys.*, **100,** 1477.
RAINERI, F. O., PERNG, B.-C., and FRIEDMAN, H. L., 1994b, *J. chem. Phys.*, **183,** 187.
RAMAKRISHNAN, T. V., and YUSSOUFF, M., 1979, *Phys. Rev.* B, **19,** 2775.
RAVICHANDRAN, S., and BAGCHI, B., 1994a, *J. phys. Chem.*, **98,** 2729; 1994b, *Ibid.*, **98,** 11242; 1994c, *J. molec. Struct.*, **327,** 247.
RAVICHANDRAN, S., ROY, S., and BAGCHI, B., 1994d, *J. phys. Chem.*, (in press).
RESAT, H., RAINERI, F. O., and FRIEDMAN, H. L., 1992, *J. phys. Chem.*, **97,** 2618; 1993, *Ibid.*, **98,** 7277.
RICE, S. A., CERJAN, C., and BAGCHI, B., 1985, *J. chem. Phys.*, **82,** 3350.
RIPS, I., and KLAFTER, J., 1988a, *J. chem. Phys.*, **88,** 3246; 1988b, *Ibid.*, **89,** 4288.
ROSENTHAL, S. J., XIE, X., DU, M., and FLEMING, G. R., 1991, *J. chem. Phys.*, **94,** 4715.
ROSSKY, P. J., and SIMON, J. D., 1994, *Nature*, **370,** 263.
ROTHSCHILD, W. G., 1984, *Dynamics of Molecular Liquids* (New York: Wiley).
ROY, S., KOMATH, S., and BAGCHI, B., 1993, *J. chem. Phys.*, **99,** 3139.
ROY, S., and BAGCHI, B., 1993a, *J. chem. Phys.*, **99,** 1310; *Ibid.*, **99,** 9938; 1994, *Ibid.*, **101,** 4150.

SIMON, J. D., 1988, *Acct. Chem. Res.*, **21,** 128; 1990, *Pure Appl. Chem.*, **62,** 2243.
SJÖGREN, L., and SJÖLANDRE, A., 1979, *J. Phys.* C, **12,** 4369.
VAN DER ZWAN, G., and HYNES, J. T., 1985, *J. Phys. Chem.*, **89,** 4181.
VIJAYADAMODAR, G. V., CHANDRA, A., and BAGCHI, B., 1989, *Chem. Phys. Lett.*, **161,** 413.
WEAVER, M. J., and MCMANIS III, G. E., 1990, *Accts. Chem. res.*, **23,** 294.
WEI, D., and PATEY, G. N., 1990, *J. chem. Phys.*, **93,** 1399; 1992, *Phys. Rev. Lett.*, **68,** 2043.
WERTHEIM, M. S., 1971, *J. chem. Phys.*, **55,** 4291.
WOLYNES, P. G., 1987, *J. chem. Phys.*, **86,** 5133; 1988, *Proceedings International Symposium on Frontiers in Science*, edited by F. F. Chan and P. G. Debrunner, (AIP Conf. Proc. No. 180), p. 39.
ZHOU, H.-X., 1993a, *Biophys. J.*, **64,** 1711; 1993b, *J. phys. Chem.*, **97,** 4216.
ZHOU, H.-X., and BAGCHI, B., 1992, *J. chem. Phys.*, **97,** 3610.
ZHOU, H.-X., BAGCHI, B., PAPAZYAN, A., and MARONCELLI, M., 1992, *J. chem. Phys.*, **97,** 9311.
ZWANZIG, R., 1963, *J. chem. Phys.*, **38,** 2766.