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# Vibrational energy relaxation, nonpolar solvation dynamics and instantaneous normal modes: Role of binary interaction in the ultrafast response of a dense liquid

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Recently instantaneous normal mode analysis has revealed an interesting similarity of the solvent dynamical influence on two rather different phenomena, namely vibrational energy relaxation (VER) and nonpolar solvation dynamics (NPSD). In this work we show that this similarity can be rationalized from a mode coupling theoretic analysis of the dynamic response of a dense liquid. The present analysis demonstrates that VER and the initial NPSD are coupled primarily to the binary part of the frequency dependent frictional response of the liquid. It is found that for strong solute-solvent interaction, the initial decay of nonpolar solvation dynamics can proceed with time constant less than 100 fs. In addition, a very good agreement between the calculated and the simulated VER rates have been obtained for a large range of frequency. © 1998 American Institute of Physics. [S0021-9606(98)50112-2]

## I. INTRODUCTION

Considerable progress has been made in recent years in understanding the influence of solvent dynamics on a large number of chemical relaxation processes in solution. It has been discovered that not only many elementary chemical reactions, such as electron transfer reactions<sup>1-4</sup> and isomerization dynamics<sup>5</sup> occur with great rapidity, but other chemical processes such as solvation of a newly created charge distribution can also proceed with subpicosecond time scale.<sup>6-28</sup> These discoveries have led to renewed activity in many branches of liquid phase chemistry. For example, it has been shown that ultrafast solvation can have profound influence on such commonly assumed slow process as ionic conductivity of an electrolyte solution.<sup>29-31</sup> Theoretically, attempts have been made to rationalize the experimental results by not only using the standard methods of time dependent statistical mechanics, but new methods have also been invented. One such method is the study of the instantaneous normal modes (INM) to understand the short-time response of a dense liquid.<sup>32-44</sup> INM has been used to study solvation dynamics,<sup>35</sup> far-infrared (FIR) absorption spectrum<sup>45</sup> and more recently vibrational energy relaxation.<sup>36,44</sup>

The motivation of the present work comes from the following facts. Recently Stratt and co-workers have reported the surprising result that the rate of the vibrational energy relaxation (VER) and the nonpolar solvation dynamics (NPSD) in a nonpolar liquid both are dominated by the dynamical events only of binary interactions (or modes).<sup>38</sup> While the important role of binary collisions in VER has been discussed earlier,<sup>46-50</sup> the same for NPSD has not been anticipated before. The objective of this note is to demonstrate that such similarity can be understood from an entirely

different theoretical framework, that is, the mode coupling theory.<sup>51,52</sup> The latter provides a reliable description of the frequency (or time) dependent response of the liquid.

There is, however, a more fundamental aspect of this problem. Several recent studies on solvation dynamics have found a nearly universal ultrafast component in the 50–100 fs range in many solvents.<sup>13,14,26-28</sup> The presence of such components in water and acetonitrile has been rationalized in various theories.<sup>23</sup> It is the presence of such ultrafast components in higher normal alcohols (ethanol-butanol), reported recently by Joo *et al.*,<sup>26</sup> that deserves special attention. These authors studied the solvation dynamics of a large dye molecule in alcohols by using three pulse photon echo peak shift (3PEPS) measurements and they found that 30%–60% of the decay of the total solvation energy correlation function is carried out by an ultrafast Gaussian component with a time constant ( $\tau_G$ ) less than 100 fs. Joo *et al.*,<sup>26</sup> have also found that the presence of such an ultrafast component in alcohols (methanol-butanol) is rather *generic* in nature. These observations were different from the experimental results of Horng *et al.*<sup>27</sup> who studied the *polar* response of the solvent to an instantaneously created charge distribution and found no such ultrafast component. The scenario has become even more interesting by a very recent experimental studies of Ernsting and co-workers on the solvation dynamics of LDS 750 dye in solvents like chloroform and acetonitrile.<sup>53</sup> In this work Ernsting and co-workers<sup>53</sup> argued that the experimentally observed fluorescence Stokes' shift for the dye molecule at times less than 70 fs may be attributed to various intramolecular relaxation processes such as isomerization and/or vibrational energy relaxation.<sup>53</sup> Recently, we carried out a theoretical investigation on the *polar* solvation dynamics in these monohydroxy alcohols<sup>54</sup> and found also that there is no ultrafast component in the *polar solvent response* with  $\tau_G \leq 100$  fs present in these solvents except in methanol. In the same work, we have also shown that a microscopic theory based on a realistic model for solvent dynamic re-

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sponse can give rise to a time constant of 150–200 fs for nonpolar solvation which is, again, higher than that reported by Joo *et al.*<sup>26</sup>

A possible interpretation of this ultrafast component has been provided by instantaneous normal mode analysis which finds free inertial motion of the solvent molecules responsible for this component. The INM studies on solvation dynamics by Ladanyi and Stratt<sup>35</sup> have revealed a nearly universal mechanism for the solvation of an excited solute in a solvent, irrespective of the nature of the solute–solvent interaction (nonpolar, dipolar or ionic). According to the picture provided by Ladanyi and Stratt,<sup>35(b)</sup> the solvation is dominated by the simultaneous participation of the nearest-neighbor solvent molecules where the solvent libration is usually the most efficient route to the solvation. Recently, Skinner and co-workers<sup>55</sup> have presented an interesting analysis of the nonpolar solvation dynamics where energy relaxation in the range of 100 fs was observed. In this work, the ultrafast component arises from the solute–solvent two-particle translational dynamics in the cage of the other solvent molecules. Thus, here also the binary part plays the dominant role.

In our earlier study of nonpolar solvation dynamics<sup>54,56</sup> we did not consider the contribution of the binary part to the solvation energy explicitly—the binary part was included only in the frictional response. The situation for nonpolar solvation could be quite different from polar solvation. In the latter energy relaxation may be dominated by the coupling of the polar solute's electric field to the solvent polarization whose dynamics is controlled by the collective density relaxation of the solvent. This density relaxation of course contains the binary component. Note that the above separation is somewhat arbitrary because the total energy of a polar solute may also contain a significant nonpolar contribution. The separation into binary and the rest—the correlated contribution—to the energy, becomes necessary when the short-range part of the intermolecular interaction makes a dominant contribution to the total energy and this is certainly the case for nonpolar solvation. An important point to note that in time dependent fluorescence Stokes shift experiments on polar solutes in polar solvents, the nonpolar part may not make a large contribution because this part may not change significantly upon excitation.

In this work we present an analytic study of the importance of the binary part to the nonpolar solvation dynamics by using the ideas of the mode-coupling theory. A particular advantage of this approach is that it explicitly separates both the energy and the force into a binary part from short range interactions and a collective part from the correlated dynamics involving many particles. This approach has been rather successful in dealing with the dynamics of dense liquids. We report the results of theoretical analysis of nonpolar solvation dynamics, vibrational energy relaxation rate and frequency dependent friction. We find that 60% of the total decay of the nonpolar solvation energy correlation function with a time constant of  $\sim 100$  fs is carried out by the binary interaction part only. The important point here is that both of them are controlled almost entirely by the binary part of the frequency dependent friction.

The vibrational energy relaxation has a long history.<sup>46–49,57–60</sup> Several theoretical studies on vibrational energy relaxation have been carried out by invoking two basic models—the isolated binary collision (IBC) model in which the collision frequency is modified by the liquid structure, and the weak coupling model where the vibrational motion of the molecule weakly couples to the rest (translational and rotational) degrees of freedom so that a perturbative technique can be employed. The IBC model has been developed by Herzfeld, Litovitz, and Madigosky<sup>49,50</sup> and the VER rate for two level systems is assumed to be given by  $\tau_{ij}^{-1} = P_{ij}\tau_c^{-1}$ , where  $\tau_c^{-1}$  is the collision frequency and  $P_{ij}$  is the probability per collision that a transition from level  $i$  to level  $j$  will take place. Note that  $P_{ij}$  is independent of density but does depend on temperature whereas  $\tau_c$  depends both on these two state parameters.

In the present work, we use the friction from the mode coupling theory to calculate the VER rate in dense liquids. The agreement between the theoretical predictions and computer simulation results<sup>60</sup> is excellent over a large frequency range. The energy relaxation is found to couple only to the initial part of the binary component of the total friction. This is in agreement with the conventional wisdom. The calculations presented here, however, are analytic and no adjustable parameter has been used.

A large number of theoretical studies have been carried out recently to calculate the density of states (DOS) in liquid with the hope that it will help in understanding the liquid state dynamics.<sup>61–65</sup> The density of states are generally expressed in terms of two quantities—the averaged and the weighted density of states. The averaged density of states (ADOS) could be related to the velocity autocorrelation function by using harmonic approximation.<sup>61</sup> The weighted density of states (WDOS), as shown recently by Stratt *et al.*,<sup>36</sup> is related directly to the frequency dependent friction. A study of WDOS is also presented in this article.

The organization of the rest of the paper is as follows. Section II A contains the theory for the calculation of the frequency dependent friction. Section II B describes the theoretical details of the nonpolar solvation dynamics of a Lennard-Jones particle in Lennard-Jones fluid. Section II C contains the discussion on vibrational energy relaxation. In Sec. II D we present the theory for the calculation of weighted density of states in a liquid. The results are presented in Sec. III. We conclude the paper with a brief summary in Sec. IV.

## II. THEORETICAL FORMULATION

### A. Frequency dependent friction

The calculation of the frequency dependent friction is rather involved. For the present purpose, the main interest is the high frequency limit of this friction. As shown below, this can be obtained in two different ways. Both the approaches generate numerically similar results, although the semiempirical approach is much simpler. In the following both the approaches are outlined.

Both in the modern kinetic theory<sup>51</sup> and in the sophisticated mode coupling theory<sup>52</sup> the frequency ( $z$ ) dependent

total friction,  $\zeta(z)$  of a dense liquid is assumed to be given by the combination of three terms. These are the binary collision term ( $\zeta_B(z)$ ), the density fluctuation term ( $\zeta_{\rho\rho}(z)$ ) and the transverse current term ( $\zeta_{tt}(z)$ ). However, the contribution of these terms are not additive. The final expression is given by the following relation:<sup>52</sup>

$$\frac{1}{\zeta(z)} = \frac{1}{[\zeta_B(z) + \zeta_{\rho\rho}(z)]} + \frac{1}{\zeta_{tt}(z)}. \quad (1)$$

Note here that the binary friction,  $\zeta_B(z)$  is determined by the short range interactions between the solute and the solvent molecules whereas both the  $\zeta_{\rho\rho}(z)$  and  $\zeta_{tt}(z)$  are governed by the relatively long range interactions.

We first describe the calculation of  $\zeta_{\rho\rho}(t)$ . This contribution originates from the coupling of the solute motion to the collective density fluctuation of the solvent through the solute-solvent two particle direct correlation function. The expression for  $\zeta_{\rho\rho}(t)$  is as follows.<sup>52,66</sup>

$$\zeta_{\rho\rho}(t) = \frac{\rho k_B T}{[m(2\pi)^3]} \int d\mathbf{q}' (\hat{q} \cdot \hat{q}')^2 q'^2 [F^s(q', t) - F^0(q', t)] [c_{12}(q')]^2 F(q', t), \quad (2)$$

where  $k_B$  is the Boltzmann constant and  $T$  the temperature in Kelvin.  $F^s(q, t)$  is the dynamic structure factor of the solute and  $F^0(q, t)$  represents the inertial part of the dynamic structure factor of the solute.  $c_{12}(q)$  denotes the wave number ( $q$ ) dependent two particle direct correlation function.  $F(q, t)$  is the dynamic structure factor of the solvent. An interesting aspect of the above equation is that it accounts for the microscopic distortion of the solvent around the solute through the product  $c_{12}(q)F(q, t)$ . For particles interacting via Lennard-Jones interaction,  $c_{12}(q)$  can be obtained by employing the well-known WCA theory<sup>67,68</sup> which requires the solution of the Percus-Yevick equation for the binary mixture.<sup>69</sup> The latter is obtained in the limit of zero solute concentration. The calculational procedures of the other quantities have been described in detail elsewhere<sup>66</sup> and thus we discuss them briefly here.

We use the following expression of solvent dynamic structure factor,  $F(q, t)$ :

$$F(q, t) = \mathcal{L}^{-1} \left[ \frac{S(q)}{z + \frac{\langle \omega_q^2 \rangle}{z + \frac{\Delta_q}{z + \tau_q^{-1}}}} \right], \quad (3)$$

where the solvent dynamic structure factor in the frequency ( $z$ ) plane is obtained from Mori continued fraction expansion truncated at second order.<sup>70</sup>  $\mathcal{L}^{-1}$  denotes the Laplace inversion which is performed numerically by using the Stehfest algorithm.<sup>71</sup>  $S(q)$  is the static structure factor of the solvent and is calculated from the solution of the Percus-Yevick equation for pure liquids.<sup>72,73</sup>  $\langle \omega_q^2 \rangle = [k_B T q^2 / m S(q)]$  and  $\tau_q^{-1} = 2\sqrt{(\Delta_q / \pi)}$ ,  $\Delta_q = \omega_1^2(q) - \langle \omega_q^2 \rangle$  where,  $\omega_1^2(q)$  is the second moment of the longitudinal current correlation function. The other equations and parameters necessary for the calculation of  $F(q, t)$  are given in Ref. 52.

Next we describe the expression for the self-dynamic structure factor,  $F^s(q, t)$ . The expression of  $F^s(q, t)$  is shown to be given by<sup>70,74</sup>

$$F^s(q, t) = \exp \left[ \frac{-q^2 k_B T}{m \zeta_0} \left( t + \frac{1}{\zeta_0} (e^{-t\zeta_0} - 1) \right) \right], \quad (4)$$

where  $\zeta_0 = \zeta(z=0)$ , the latter has been calculated self-consistently from Eq. (1). In the expression of  $F^s(q, t)$  using the zero frequency value of the friction is clearly an approximation. It is the time dependent friction which should be used to obtain the correct result. But doing an infinite-loop calculation with the time dependent friction is highly non-trivial. Note that the form of the self part is accurate both in the short and in the long time, but it precludes any nonexponential behavior of  $F^s(q, t)$  that it may exhibit in the intermediate time. However, this can only be a minor limitation of the present work,<sup>29</sup> because, this nonexponentiality at the intermediate times is expected to be small for tracers with sizes smaller than the solvent molecules.<sup>70,74</sup> Assuming the zero frequency limit does not introduce much error as we know that the major contribution of  $\zeta_{\rho\rho}(t)$  to the total friction is in the long time limit. The inertial part of the self dynamic structure factor,  $F^0(q, t)$  is given by<sup>52</sup>

$$F^0(q, t) = \exp \left( -\frac{k_B T}{m} \frac{q^2 t^2}{2} \right). \quad (5)$$

The third contribution in Eq. (1) comes from  $\zeta_{tt}(z)$  which originates from the coupling of the solute's motion with the transverse mode of the collective density fluctuation. The calculation of  $\zeta_{tt}(z)$  is highly nontrivial. However, we do not need  $\zeta_{tt}(z)$  in the present calculation since it has been shown explicitly in Ref. 66 that the  $\zeta_{tt}$  contribution becomes negligible in a solvent at high density with a solute of comparable size.

### B. Microscopic expression for binary friction

The quantity which is particularly relevant in the present work is the binary part of the friction,  $\zeta_B(z)$ . This contribution originates from the instantaneous two-body collision between the solute and solvent particles. Since these collisional events are always associated with the ultrashort time (time scale  $\leq 100$  fs) dynamics of the medium, the time dependence of the binary friction could be well approximated by the following Gaussian decay function:<sup>51</sup>

$$\zeta_B(t) = \Omega_0^2 \exp[-(t/\tau_B)^2], \quad (6)$$

where  $\tau_B$  is the time constant associated with the above binary Gaussian relaxation.  $\Omega_0$  is the Einstein frequency of the solute in the solvent cage. This quantity can be evaluated from the solute-solvent radial distribution function  $g_{12}(r)$  and the interaction potential ( $v_{12}(r)$ ) between them as follows:<sup>52,68</sup>

$$\Omega_0^2 = \frac{4\pi\rho}{3m} \int_0^\infty dr r^2 g_{12}(r) \nabla_r^2 v_{12}(r), \quad (7)$$

where  $m$  is the mass of a solute particle and  $\rho$  is the density of the solvent. We need the expression for the time constant,

$\tau_B$  to calculate  $\zeta_B(t)$  from Eq. (6). The expression for  $\tau_B$  can be derived from the definition of  $\zeta(t)$  by using the short time expansion and is given by<sup>52</sup>

$$\begin{aligned} \Omega_0^2/\tau_B^2 &= (\rho/3m)^2 \int d\mathbf{r} (\nabla^\alpha \nabla^\beta v_{12}(\mathbf{r})) g_{12}(\mathbf{r}) \\ &\quad \times (\nabla^\alpha \nabla^\beta v_{12}(\mathbf{r})) + (1/6\rho) \\ &\quad \times \int [d\mathbf{q}/(2\pi)^3] \gamma_{d12}^{\alpha\beta}(\mathbf{q}) [S_{12}(q) - 1] \\ &\quad \times (q) \gamma_{d12}^{\alpha\beta}(\mathbf{q}), \end{aligned} \quad (8)$$

where summation over repeated indices is implied. The other quantities in Eq. (8) are described in Ref. 52. It is clear from the above expression that though Eq. (8) provides an accurate estimation of  $\tau_B$ , its implementation requires extensive numerical work.

In the following we derive a simpler (although approximate) expression for  $\zeta_B(t)$ . First, note that the expression for the same time force-force correlation function is given exactly by

$$C_{FF}(t=0) = [4\pi\rho k_B T] \times \int_0^\infty dr r^2 g_{12}(r) \nabla_r^2 v_{12}(r). \quad (9)$$

This is determined by the binary interaction terms only and is proportional to the Einstein frequency. Thus, a straightforward generalization to the time dependence of the binary part of the force-force time correlation function would be<sup>55</sup>

$$C_{FF}^B(t) = [4\pi\rho k_B T] \times \int_0^\infty dr r^2 G_{12}(r,t) \nabla_r^2 v_{12}(r), \quad (10)$$

where  $G_{12}(r,t)$  is the distinct part of the van Hove time correlation function, defined by  $G_{12}(r,t) = \langle \delta[r-r(t)] \rangle$ , where  $r(t)$  is the time dependent separation between the solute and a solvent molecule.<sup>68</sup> Note that Eq. (10) is approximate but sensible in the short time. If one now assumes that the initial decay of the correlation function is given by  $C_{FF}^B(t) = C_{FF}^B(t=0) \exp[-(t/\tau_F^B)^2]$  then one obtains the following expression for the Gaussian relaxation time constant:

$$\tau_F^B = \sqrt{\frac{-2C_{FF}^B(t=0)}{\ddot{C}_{FF}^B(t=0)}}, \quad (11)$$

where (and hereafter) the symbol *double dot* signifies the double derivative of the function in question with respect to time. This quantity is given by the following expression:

$$\ddot{C}_{FF}^B(t) = (4\pi\rho k_B T) \times \int_0^\infty dr r^2 \ddot{G}_{12}(r,t) \nabla_r^2 v_{12}(r). \quad (12)$$

We now derive an expression for  $\ddot{G}_{12}(r,t)$  which is valid at short times. From the definition of  $G_{12}(r,t)$ , the expression for  $G_{12}(r,t+\Delta t)$  can be written as<sup>75</sup>

$$\begin{aligned} G_{12}(r,t+\Delta t) &= \langle \delta[r-r(t+\Delta t)] \rangle \\ &= \langle \delta[r-r(t) - \Delta r(t)] \rangle. \end{aligned} \quad (13)$$

Expanding the above  $\delta$ -function with respect to powers of  $\Delta r$ , we obtain

$$\begin{aligned} G_{12}(r,t+\Delta t) &= \langle \delta[r-r(t)] \rangle - \Delta r \left\langle \frac{\partial}{\partial r} \delta[r-r(t)] \right\rangle \\ &\quad + \frac{(\Delta r)^2}{2} \left\langle \frac{\partial^2}{\partial r^2} \delta[r-r(t)] \right\rangle - \dots. \end{aligned} \quad (14)$$

We now define the increment,  $\Delta G_{12}(r,t)$ , over  $G_{12}(r,t)$  as follows:

$$\Delta G_{12}(r,t) = G_{12}(r,t+\Delta t) - G_{12}(r,t), \quad (15)$$

which, after using Eq. (14) and the definition of  $G_{12}(r,t)$ , produces the following expression:

$$\begin{aligned} \Delta G_{12}(r,t) &= -\Delta r \left\langle \frac{\partial}{\partial r} \delta[r-r(t)] \right\rangle \\ &\quad + \frac{(\Delta r)^2}{2} \left\langle \frac{\partial^2}{\partial r^2} \delta[r-r(t)] \right\rangle - \dots. \end{aligned} \quad (16)$$

Now, since  $\Delta r \rightarrow 0$  as  $\Delta t \rightarrow 0$ , we neglect all the terms in Eq. (16) containing  $(\Delta r)^2$  and higher powers of it and obtain the following expression for  $\Delta G_{12}(r,t)$ :

$$\Delta G_{12}(r,t) = -\Delta r(t) \nabla_r G_{12}(r,t). \quad (17)$$

Now in the same way if we define the increment over  $\Delta G_{12}(r,t)$  as

$$\Delta \Delta G_{12}(r,t) = \Delta G_{12}(r,t+\Delta t) - \Delta G_{12}(r,t), \quad (18)$$

where  $\Delta G_{12}(r,t+\Delta t)$  is given by

$$\begin{aligned} \Delta G_{12}(r,t+\Delta t) &= -[\Delta r(t+\Delta t)] \\ &\quad \times \left[ \frac{\partial}{\partial r} \langle \delta(r-r(t) - \Delta r(t)) \rangle \right]. \end{aligned} \quad (19)$$

Now expanding the above expression in the same way as done in Eq. (14) and neglecting terms containing  $(\Delta r)^2$  and higher powers of  $(\Delta r)$ , also taking into consideration the fact that the average velocity is zero, we arrive at the following exact expression:

$$\ddot{G}_{12}(r,t) = -\ddot{r}(t) \nabla_r G_{12}(r,t). \quad (20)$$

We now define an effective force,  $F(r)$  as  $F(r) = \mu \ddot{r}(t)$ , where  $\mu$  is the reduced mass of the solute-solvent composite system and also use the equality  $G_{12}(r,t=0) = g_{12}(r)$  to rewrite Eq. (20) in the following form:

$$\ddot{G}_{12}(r,t=0) = -\frac{F(r) \nabla_r g_{12}(r)}{\mu}. \quad (21)$$

In the next step, we need to calculate the force,  $F(r)$  acting on the solute particle. There are two alternative procedures to obtain this force. First, one may approximate this by taking the derivative of the Kirkwood's *potential of mean force*,  $W(r)$  related to  $g(r)$  by<sup>68</sup>  $W(r) = -k_B T \ln g(r)$ . This is the form used by Skinner and co-workers.<sup>76</sup> However, this is inaccurate in the very short time where force is determined by the direct pair wise binary interactions. Consequently, the expression for  $F(r)$  is assumed to be given by

$$F(r) = -\nabla_r v_{12}(r). \quad (22)$$

Note that at long times one should use the potential of mean force to obtain  $F(r)$ .

In order to calculate the Gaussian time constant  $\tau_F^B$  from Eq. (11), we need the expression for  $\ddot{G}_{FF}^B(t=0)$ . Following the same procedure as outlined above, the following analytic expression has been derived:

$$\begin{aligned} \ddot{C}_{FF}^B(t=0) &= [4\pi\rho k_B T] \int_0^\infty dr r^2 \frac{\nabla_r g_{12}(r)}{\mu} \nabla_r v_{12}(r) \nabla_r^2 v_{12}(r). \end{aligned} \quad (23)$$

We find that the time constants predicted by these two alternative methods [from Eqs. (8) and (11)] differ only by about 10% from each other. While the first one is expected to be more accurate, the second approach is far simpler and can be used to obtain an estimate of the force–force time correlation function.

### C. Nonpolar solvation dynamics

Extensive experimental studies on the time dependent progress of solvation of excited nonpolar solute in nonpolar solvent have been performed in recent years.<sup>77–79</sup> Various theoretical studies<sup>55,56,76</sup> have already explained many of these experimental observations. In this section we try to develop a theory which describes the time dependent solvent response at a very short time. The work presented here has been motivated partly by the recent work of Skinner and co-workers.<sup>55</sup> Our main concern here is the normalized solvation energy–energy time correlation function ( $S_{NP}(t)$ ) of the solute with the nonpolar interaction as the only source of energy. The expression for  $S_{NP}(t)$  is given by

$$S_{NP}(t) = \frac{C_{EE}(t)}{C_{EE}(t=0)}, \quad (24)$$

where  $C_{EE}(t)$  is the solvation energy time correlation function. If  $v_{12}(r)$  denotes the interaction energy between the solute and a solvent molecule, then the instantaneous energy of the solute can be written as

$$E_{1,\text{solv}}(t) = \sum_j v_{1j}(r_{1j}(t)), \quad (25)$$

where the summation runs over all the  $j$  solvent molecules. The calculation of the corresponding energy–energy time correlation function is rather complicated. An approximate expression for this has been derived recently by Skinner and co-workers.<sup>55</sup> In the following we present an alternative expression which we believe is, at least, equally valid. The treatment is entirely analytical and is accurate both at short and long times. The results obtained are quite similar to those of Skinner and co-workers.<sup>55</sup>

As in the calculation of the force–force time correlation function we assume that the energy–energy time correlation function can be separated into the short time binary part and a long time collective part. The binary part relaxes on a faster time scale while the slow collective part which is coupled to the solvent density fluctuation, relaxes on a much longer time scale. Thus the expression of the energy time correlation function is assumed to be given by

$$C_{EE}(t) = C_{EE}^B(t=0) \exp[-(t/\tau_E^B)^2] + C_{\rho\rho}(t), \quad (26)$$

where we have already assumed that the binary part is Gaussian. The expression for the collective density fluctuation part ( $C_{\rho\rho}(t)$ ) is obtained from the density functional theory and is given by<sup>56</sup>

$$C_{\rho\rho}(t) = \frac{(k_B T)^2 \rho}{6\pi^2} \int_0^\infty dq q^2 c_{12}^2(q) F^s(q,t) F(q,t). \quad (27)$$

In order to calculate  $C_{\rho\rho}(t)$  by using the above equation we use the same expressions of  $F(q,t)$  and  $F^s(q,t)$  as given by Eqs. (3) and (4), respectively.  $c_{12}(q)$  is obtained by using the WCA approximation, as before.

The above expression has a simple physical meaning. The binary part arises from the relaxation due to the direct interaction of two particles while the cage around the solute (whose energy is being considered) remains fixed. The second term, on the other hand, involved the relaxation of the cage itself.

We next derive a microscopic expression of the time constant associated with the binary part of the solvation energy,  $\tau_E^B$ . We follow the same steps as followed in the calculation of the force–force time correlation function. The expression for the time constant is given by

$$\tau_E^B = \sqrt{\frac{-2C_{EE}^B(t=0)}{\ddot{C}_{EE}^B(t=0)}}, \quad (28)$$

where

$$C_{EE}^B(t=0) = 4\pi\rho \int_0^\infty dr r^2 [v_{12}(r)]^2 g_{12}(r), \quad (29)$$

and

$$\ddot{C}_{EE}^B(t=0) = \frac{4\pi\rho}{m} \int_0^\infty dr r^2 [v_{12}(r)]^2 \nabla_r g_{12}(r) \nabla_r v_{12}(r). \quad (30)$$

Note that the time zero limit of Eq. (26) gives the mean square energy fluctuation of the nonpolar solvation energy. This is an approximate expression. The exact expression would involve three particle ( $g_3(r)$ ) and higher order correlation functions, as discussed by Skinner and co-workers.<sup>55</sup> However, the contribution of these higher order correlation terms can be absorbed in the collective density fluctuation part ( $C_{\rho\rho}(t)$ ) and hence, the  $t=0$  limit of Eq. (26) is expected to provide the mean square fluctuation of the nonpolar solvation energy without any significant error.

We discuss the theoretical results obtained by using Eqs. (24), (26), and (27) in Sec. III.

### D. Vibrational energy relaxation

In order to clarify the similarity between VER and NPSD, we shall consider a very simple system. We consider a diatomic solute molecule in a monatomic solvent interacting through Lennard-Jones interaction. This is also the system considered by Stratt and co-workers.<sup>36</sup> For vibrational energy relaxation in the low lying vibrational levels, it is reasonable to assume that the vibration is harmonic. Under

these conditions, it has been shown that the time constant of vibrational energy relaxation can be given by the following general Landau–Teller expression:<sup>80</sup>

$$\frac{1}{T_1} = \frac{\zeta_{\text{real}}^{\text{bond}}(\omega_0)}{\mu}, \quad (31)$$

where  $\mu$  is the reduced mass of the system comprising the vibrating bond.  $\zeta_{\text{real}}^{\text{bond}}(\omega_0)$  is the frequency dependent bond friction evaluated at the harmonic frequency of the bond. Molecular dynamics simulation studies of Berne *et al.*<sup>60(a)</sup> have shown that in the free draining limit (that is, where the cross correlations between the solvent forces on each atom of the diatomic is neglected),  $\zeta_{\text{real}}^{\text{bond}}(\omega_0) = 0.5 \times \zeta_{\text{real}}(\omega_0)$ , where  $\zeta_{\text{real}}(\omega_0)$  is the friction experienced by one of the atoms of the vibrating homonuclear diatomic. Here the frequency dependent friction has been obtained from the mode coupling theory described elsewhere in more detail.<sup>51,52,66</sup>

### E. Weighted density of states of a liquid

The weighted density of states (WDOS) is directly related to the friction through the following expression:<sup>36</sup>

$$\zeta(\omega) = \int_0^\infty d\omega' \rho_w(\omega') \frac{\cos(\omega t)}{\omega'^2}, \quad (32)$$

where  $\omega$  is the Fourier frequency and  $\rho_w(\omega)$  is the weighted density of states. Taking a Fourier transformation of the above equation, it can be written as

$$\rho_w(\omega) = \frac{2}{\pi} \omega^2 \zeta_{\text{real}}(\omega). \quad (33)$$

The most important quantity in the calculation of the VER and the WDOS is the real part of the frequency dependent total friction,  $\zeta_{\text{real}}(\omega)$ . We shall discuss the numerical results of  $\zeta_{\text{real}}(\omega)$  in the next section.

## III. NUMERICAL RESULTS

### A. Nonpolar solvation dynamics

Here we present the numerical results on nonpolar solvation dynamics calculated by using Eq. (24) in conjunction with Eqs. (26) and (27). In Fig. 1, we plot the normalized energy time correlation function,  $S_{NP}(t)$  obtained for a Lennard-Jones system at  $\rho\sigma^3 = 0.844$  and  $T^* (= k_B T / \epsilon) = 0.728$  with  $\sigma = 3.41 \text{ \AA}$ ,  $m = 40 \text{ amu}$  and  $\epsilon = 120 k_B$ . The calculation is carried out for the size and mass ratios 1. The Gaussian time constant ( $\tau_E^B$ ) obtained at this state point is 110 fs. In the same figure we have shown the decomposition of the total energy into the binary and the collective parts. It is clear from the above figure (Fig. 1) that the normalized binary relaxation part accounts for  $\sim 62\%$  of the decay of the total nonpolar solvation energy time correlation function. The remaining part is carried by the collective density fluctuation. The domination of the binary part in nonpolar solvation dynamics indicates that the nearest-neighbor participation makes the solvation ultrafast is indeed true for the nonpolar solvation dynamics.

We now comment on the time constant associated with the binary part of the solvation energy correlation function.

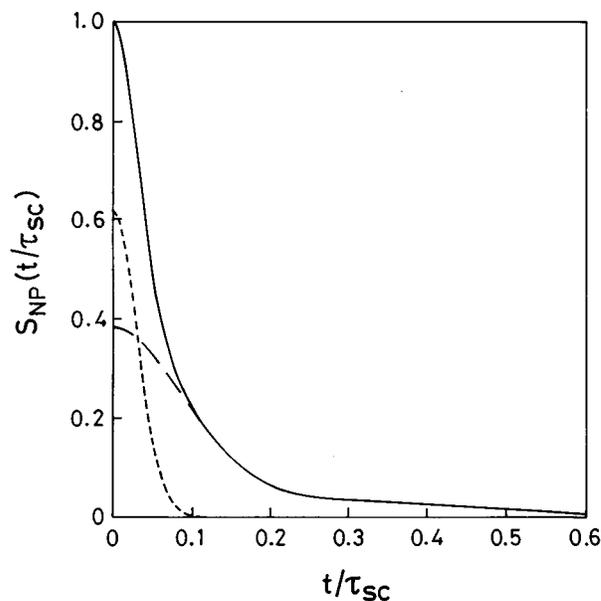


FIG. 1. A comparison between the binary and the collective components of the nonpolar solvation energy time correlation functions. The normalized nonpolar solvation energy time correlation function  $S_{NP}(t)$  is plotted as a function of time,  $t$  for the solute–solvent size ratio 1. The solid line represents the decay of the total non-polar solvation energy time correlation function. This has been calculated by using Eq. (24) of the text. The small dashed line shows the decay of the binary component and the long dashed line the decay of the collective component of the total  $S_{NP}(t)$ . The solvent considered is argon at  $T^* = 0.728$  with  $\rho^* = 0.844$ . The mass of the solute is taken as that of an argon atom. Note that the time is scaled by the quantity  $\tau_{sc} = \sqrt{(m\sigma^2/k_B T)}$ . This is equal to  $2.527 \times 10^{-12}$  s. For discussion, see the text.

For a Lennard-Jones system, the present theory gives a value of 110 fs for the binary time constant at  $\rho^* = 0.844$  and  $T^* = 0.728$ . This is in agreement with the results of Skinner and co-workers.<sup>55</sup> However, this is still larger than the fastest time scale observed experimentally by Joo *et al.*<sup>26</sup> The reason for the discrepancy may be the following. Joo *et al.*<sup>26</sup> used a huge dye molecule which may lead to specific solute–solvent interaction both in the ground and excited states. This type of specific interaction is stronger than the usual solute–solvent binary interaction. This, in turn, means the movement of the solute particle in a much deeper potential well created by the nearest-neighbor solvent molecules. This would certainly reduce the value for the binary time constant. This trend is shown in Table I where we have calculated the time constants by varying the solute–solvent  $\epsilon$  ratio

TABLE I. The time constant associated with the binary energy relaxation ( $\tau_E^B$ ) calculated at different solute–solvent  $\epsilon$  ratios. The time constants are calculated by using Eq. (28). The solute–solvent size and mass ratios are taken as unity. The solvent is argon at 120 K.

| $\epsilon_{\text{solute}}/\epsilon_{\text{solvent}}$ | $\tau_E^B$ (fs) |
|------------------------------------------------------|-----------------|
| 1                                                    | 110             |
| 2                                                    | 99              |
| 3                                                    | 90              |
| 4                                                    | 80              |
| 5                                                    | 72              |

TABLE II. The vibrational energy relaxation rates calculated by using Eq. (29). The system studied here is a homonuclear diatomic solute dissolved in Lennard-Jones argon at  $\rho^*=1.05$  and  $T^*=2.5$  with  $\sigma_{Ar}=3.41 \text{ \AA}^0$  and  $m_{Ar}=39.5$  amu. The atomic size and the atomic mass of the diatomic solute are the same as those of an argon atom. For comparison, the INM results of Stratt *et al.* (Ref. 36) and the simulation results of Berne *et al.* [Ref. 60(a)] are also shown in the same table.

| $\bar{\nu}(\text{cm}^{-1})$ | $1/T_1$ —theory( $\text{ps}^{-1}$ ) | $1/T_1$ —simulation( $\text{ps}^{-1}$ ) | $1/T_1$ —INM( $\text{ps}$ ) |
|-----------------------------|-------------------------------------|-----------------------------------------|-----------------------------|
| 39.7                        | 11.44                               | 11.26                                   | 12.69                       |
| 68.7                        | 9.8                                 | 9.64                                    | 12.5                        |
| 145.0                       | 2.6                                 | 3.16                                    | 3.26                        |
| 221.6                       | 0.4                                 | 0.99                                    | 0.05                        |

at size and mass ratios unity. The same trend has also been found by Ohmine *et al.*,<sup>81</sup> although in a different context.

## B. Vibrational energy relaxation

Next we discuss the numerical results on the vibrational energy relaxation (VER). We present the calculated rate of the vibrational energy relaxation in Table II. The system studied here is a homonuclear diatomic dissolved in Lennard-Jones argon at  $\rho^*=1.05$  and  $T^*=2.5$ . The atomic mass and size of the diatomic solute are the same as those of an argon atom. The frequency dependent bond friction is calculated from mode coupling theory. In Fig. 2, we show the comparison between the calculated friction and that obtained from the simulation studies of Straub *et al.*<sup>60(b)</sup> The plot shows that there are some oscillations present in the friction calculated from the mode coupling theory, which actually mars the otherwise good agreement. The results ob-

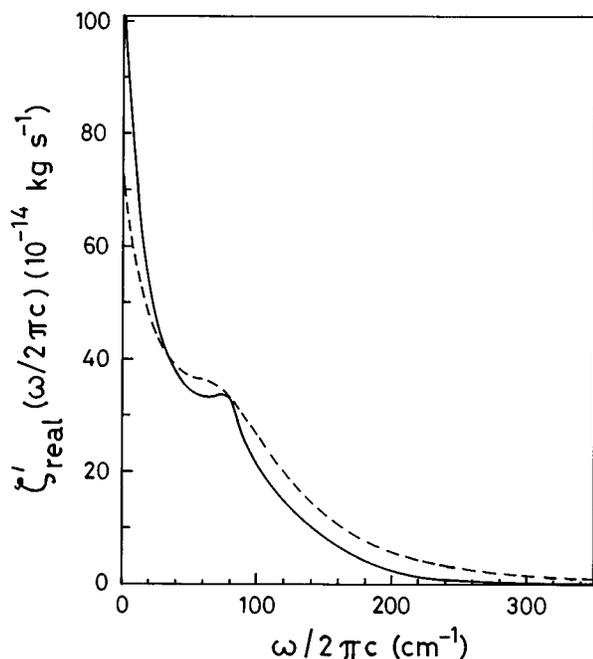


FIG. 2. The half of the real part of the calculated total friction is plotted against frequency. The calculated friction (solid line) is also compared with the simulated friction (dashed line) reported in Ref. 60(b) (Fig. 6). The solvent considered is argon at  $T^*=2.5$  with  $\rho^*=1.05$ . Note that  $\zeta'_{real}=(\zeta_{real}/2)$ .

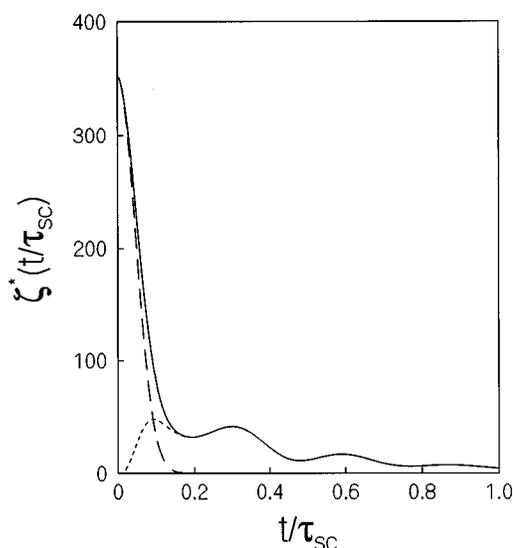


FIG. 3. A comparison between the binary and the collective components of the time dependent friction. The time dependent friction,  $\zeta^*(t/\tau_{sc})$  is plotted as a function of time. The solid line denotes the decay of the total friction with time. The long dashed line represents the decay of the binary part of the total friction and the small dashed line shows the decay of the collective part of the total friction. Note that the friction plotted here is scaled as follows:  $\zeta^*(t/\tau_{sc})=\zeta(t/\tau_{sc})\times\tau_{sc}^2/m$  where  $m$  is the mass of a solvent particle. The solvent considered is argon at  $T^*=2.5$  with  $\rho^*=1.05$ . Note that the time is scaled by the quantity  $\tau_{sc}=\sqrt{(m\sigma^2/k_B T)}$ . This is equal to  $1.3636\times 10^{-12}$  s.

tained from INM analysis by Stratt *et al.*<sup>36</sup> and those from the simulation studies of Berne *et al.*<sup>60(a)</sup> are also presented in the same table. The comparison shows that at high frequency the INM approach underestimates the rate of the vibrational energy relaxation.

In Fig. 3 we show the time dependence of this friction for a Lennard-Jones system at the reduced density  $\rho^*=1.05$  and reduced temperature  $T^*=2.5$ . This binary part decays on an extremely fast time scale and the decay is mostly over by about 200 fs. The remaining contribution from the frequency dependent friction comes from the slower collective density and transverse current relaxations of the liquid. Note that although the last two components can make significant contribution to the total zero frequency friction (which is related to the diffusion coefficient), they play no role in the short time dynamics. Since the vibrational energy relaxation of a molecule in a liquid couples only to the high frequency response of the liquid, at this high temperature ( $T^*=2.5$ ) and for all the densities studied here we find that it is primarily the binary part of the friction that contributes to the vibrational energy relaxation. The differing time scales involved in the time dependent friction is also shown in Fig. 3.

Thus, in order to obtain the solvent dependence of the VER, we need to calculate the binary part as well as the collective density part. It is clear from Eqs. (9)–(12) that this binary part is sensitive not only to the details of the interaction potential between the vibrating solute and the surrounding solvent molecules, but also to the solute–solvent radial distribution function. Since the expression for the binary friction is reliable, we find that for Lennard-Jones system, the

TABLE III. Solvent density dependence of vibrational energy relaxation rates calculated at four different frequencies. The system studied here is a homonuclear diatomic solute dissolved in Lennard-Jones atomic solvent at  $T^*=2.5$ . The diameter and the mass of an atom of the atomic liquid are taken to be the same as those of an argon atom ( $\sigma_{Ar}=3.41 \text{ \AA}^0$  and  $m_{Ar}=39.5 \text{ amu}$ ). The size and the mass of an atom of the homonuclear diatomic solute are also the same as those of an argon atom.

| $\bar{\nu}(\text{cm}^{-1})$ | $1/T_1(\text{ps}^{-1}); \rho^*=0.85$ | $1/T_1(\text{ps}^{-1}); \rho^*=0.95$ | $1/T_1(\text{ps}^{-1}); \rho^*=1.05$ |
|-----------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 39.7                        | 7.53                                 | 9.45                                 | 11.44                                |
| 68.7                        | 6.19                                 | 8.16                                 | 9.8                                  |
| 145.0                       | 1.94                                 | 2.4                                  | 2.6                                  |
| 221.6                       | 0.283                                | 0.365                                | 0.4                                  |

vibrational energy relaxation depends also on the energy parameter  $\epsilon$ .

In Table III we show the solvent density ( $\rho^*$ ) dependence of the rate of the vibrational energy relaxation at constant temperature,  $T^*=2.5$ . We have calculated the rate by using the Eq. (31) where the frequency dependent bond friction has been obtained from the mode coupling theory. The system is a homonuclear diatomic solute dissolved in Lennard-Jones argon where the mass of an atom of the diatomic solute is that of an argon atom. The results are tabulated for four different frequencies at each density. A comparative study among the density dependent VER rates clearly reveals that the rate *increases* almost linearly with density at all frequencies. The enhancement of the VER rate with density can be explained from the binary interaction picture. The frequency of the effective binary collision increases as the density increases. This, in turn, reduces the time scale of the decay of the time dependent binary friction leading to a more rapid energy transfer from one vibrational state to the other which gives rise to an overall increase in the VER rate. However, we would like to mention here that within the limited range of temperature and density investigated in this work, we find that an approximate  $\rho T^{1/2}$  dependence of the vibrational energy relaxation *rate*. This appears to be in agreement with the earlier work of Hills<sup>82</sup> reviewed elegantly by Oxtoby.<sup>46</sup>

### C. Weighted density of states

The weighted density of states is also calculated from the frequency dependent friction using the relation given in Eq. (31). Doing this we obtain the correct behavior of the weighted density of states when compared with the results of Stratt *et al.*<sup>36</sup>

## IV. CONCLUSION

Let us first summarize the main results of the paper. We have investigated the relation between the nonpolar solvation dynamics and the vibrational energy relaxation, following the findings of Stratt and co-workers<sup>35(a),35(b)</sup> that these two are intimately related. The present investigation is completely different from the earlier in a sense that the present approach is based on the mode coupling theory which provides an accurate description of both short time and long time dynamics. We have used simple expressions for the

initial decay of the force–force time correlation function and energy–energy time correlation function. The application of these expressions have been partly motivated by the mode-coupling theory and partly by the work of Skinner *et al.*<sup>55</sup> It is found that the vibrational energy relaxation is almost entirely dominated by the binary friction and is decoupled from the macroscopic friction. The nonpolar solvation dynamics has been found to be determined by the binary friction at the initial times. The slow long time decay observed from the nonpolar solvation energy time correlation function still remains slaved to the hydrodynamic motion of the solvent molecules. It is further found that the time constant and the decay of the initial nonpolar solvation energy time correlation function is determined to a large extent by the strength of the solute–solvent interaction. As shown in Table I that the Gaussian time constant of the initial decay can be easily in the order of 50–100 fs if the solute–solvent attractive interaction (parametrized by  $\epsilon$ ) is sufficiently large. This seems to substantiate our earlier argument that the nonpolar solvation dynamics can be responsible for the experimental observations of Joo *et al.*<sup>26</sup> where 30%–60% of the decay of the total solvation energy correlation function has been carried out by an ultrafast component with a time constant less than 100 fs.

We have found that the binary part seems to explain the rate of the vibrational energy relaxation, as shown in Table II. Here we have assumed that the bond between the atoms of the homonuclear diatomic is rigid and there is no coupling between the translational and rotational motions.

We have also investigated that how far one can generate the density of states from the binary part. The general features of the weighted density of states are in agreement with the INM results of Stratt and co-workers.<sup>36</sup>

In the previous theories of non-polar solvation dynamics<sup>54,56</sup> the binary part was completely ignored. This led to the conclusion that the initial part of the nonpolar solvation energy time correlation function decays with a time constant of 150–200 fs. It is shown in this work that the binary part can lead to the initial decay with Gaussian time constant,  $\tau_G \sim 50$  fs. This is in agreement with the INM analysis of Stratt and co-workers<sup>35,44</sup> and simulation results of Skinner and co-workers.<sup>59</sup>

Lastly, the fair agreement obtained between the theoretical and the simulated rates of VER suggest that the mode coupling theoretic approach to short time dynamics is reliable. In a future publication, we shall present a more detailed investigation of the temperature and the solvent density dependence of the vibrational energy relaxation rate.

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