Stochastic Description of Vibrational Energy Relaxation in Fluids

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Vibrational energy relaxation of a diatomic solute in a liquid solvent is investigated by means of Langevin equation for the vibrator energy with the stochastic power source characterized by an exponential time correlation function. The memory effects included via the stochastic power source allow one to explain the behavior of the mean square energy fluctuations on short and long time scales that was obtained from molecular dynamics simulations.

Key words: Langevin equation, nonlinear interaction, vibrational energy relaxation, energy fluctuations, time correlation functions, molecular dynamics

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1 Introduction

Vibrational energy relaxation (VER) is a process of energy transfer from vibrationally excited molecules to their environment. This process is involved in many chemical reactions in gas and liquid phases\cite{1,2} and represents the basic mechanism for activation of reactants and stabilization of products during thermal chemical reactions. Therefore, great experimental and theoretical efforts have been expended to get a quantitative understanding about the energy exchange between the vibrationally excited solute and a bath gas or solvent \cite{3–6}.

The binary collision theory (BCT) \cite{7,8} is based on the assumption that VER in liquids is governed like in gas phase by independent collisions of the solute with bath molecules and was initially suggested for describing VER in gas phase. It was criticized by Zwanzig \cite{9} on the basis of the argument that correlations between random forces inherent to liquids strongly contradict underlying principles of the BCT. Although this criticism was refused \cite{10} because of small duration of hard collisions that are able to significantly change the energy of the excited solute molecule and papers supporting the BCT are regularly published \cite{5,6,11–14}, there are still many unclear points concerning the mechanisms of the energy exchange during VER.

As a rule, the frequencies of the solute vibrations are much higher than the solute characteristic frequencies and the energy transfer occurs via strongly nonlinear solute–solvent interactions. Directly these interactions can hardly be taken into account in analytical considerations. One of the possibilities to deal with complex nonlinear systems consists in employing their stochastic characteristics.

After Zwanzig’s work \cite{9}, force time correlation functions are widely used for describing VER in fluids \cite{3–6,14–18}. These functions address vibrational relaxation to stochastic equilibrium characteristics.
of the solute–solvent system. The stochastic master equation approach [19,20] serves as a firm basis for investigating the energy exchange in gas phase solvents. In this paper we use the generalized Langevin equation to consideration the stochastic characteristics of intermolecular energy exchange in fluids. The energy relaxation rates as well as evolution of the second moment of energy fluctuations are investigated.

The paper is organized as follows. The next section is devoted to Langevin equation for energy fluctuations and its solutions. In Sec. 3 equilibrium molecular dynamics (MD) simulations and their results are described and discussed. The last section concludes.

2 Generalized Langevin equation for energy fluctuations

The system consisting of a solute with a vibrational degree of freedom and $N$ solvent molecules can be considered as a stochastic system with internal noise [21]. The solvent is supposed to be in equilibrium at temperature $T$ and number density $\rho$.

In the first approximation the evolution equation for VER of the solute can be written as a Langevin equation

$$\frac{d\Delta E(t)}{dt} = -\gamma \Delta E(t) + N(t),$$

where

$$\Delta E(t) = E(t) - \langle E \rangle$$

is the deviation of the solute vibrational energy $E(t)$ at time $t$ from its mean value $\langle E \rangle$. $\gamma$ is a damping constant, and $N(t)$ is the power of a stochastic force that acts on the vibrational coordinate of the solute.

The stochastic properties of $N(t)$ can be defined by its mean value and the two-time correlation function

$$\langle N(t) \rangle = 0,$$

$$\langle N(t_1)N(t_2) \rangle = A \exp\{-\alpha|t_2 - t_1|\},$$

The latter is a symmetric function with respect to time interval $(t_2 - t_1)$. According to this definition, the stochastic power source involves memory effects on time intervals of the order of $\alpha^{-1}$. Angular brackets are used for the equilibrium ensemble averaging. The normalization constant $A$ is determined below by the vibrator energy mean square fluctuations.

The conventional Langevin equation is characterized by $\delta$-correlated random force. Eq. (4) leads to generalization of this equation. According to the fluctuation-dissipation theorem [21] the first term in the left hand side of Eq. (1) has to be written in the integral representation to be consistent with Eq. (4). However, for the sake of simplicity we investigate the memory effects through Eq. (4) only for the price of artificial decomposing the process into two subprocesses on the short and long time scales.

Eqs. (1) and (2) lead to the exponential time decay of the mean energy deviation:

$$\langle \Delta E(t) \rangle_0 = \Delta E_0 e^{-\gamma t}, \quad \Delta E_0 = E_0 - \langle E \rangle.$$  (5)

Angular brackets with subscript 0 stand for the ensemble averaging at time $t$ under the condition that initially the vibrator energy deviation from its equilibrium value is equal to $\Delta E_0$.

The evolution of the mean square energy deviation is described by the equation [22]

$$\langle (\Delta E(t))^2 \rangle_0 = (\Delta E_0)^2 e^{-2\gamma t}$$

$$+ e^{-2\gamma t} \int_0^t \int_0^t e^{\gamma(t_1+t_2)} \langle N(t_1)N(t_2) \rangle dt_1dt_2,$$

which in view of Eq. (4) can be rewritten as

$$\langle (\Delta E(t))^2 \rangle_0 = (\Delta E_0)^2 e^{-2\gamma t}$$

$$+ e^{-2\gamma t} \int_0^t \int_0^{t_1} e^{\gamma(t_1+t_2)} A e^{-\alpha(t_1-t_2)} dt_1dt_2$$

$$+ e^{-2\gamma t} \int_0^t \int_t^{t_1} e^{\gamma(t_1+t_2)} A e^{-\alpha(t_1-t_2)} dt_1dt_2.$$  (6)

After some algebra one can find
\[
\langle [\Delta E(t)]^2 \rangle_0 = (\Delta E_0)^2 e^{-2\alpha t} + \frac{A\alpha}{\gamma(\alpha^2 - \gamma^2)}(1 - e^{-2\gamma t}) - \frac{A}{\alpha^2 - \gamma^2}(1 + e^{-2\gamma t} - 2e^{-(\alpha + \gamma)t}).
\] (7)

At sufficiently large time \( t \to \infty \), the vibrator looses the information about its initial state and its mean energy fluctuations are determined [23] by the heat capacity \( C_v \):
\[
\langle [\Delta E(\infty)]^2 \rangle = \langle [\Delta E]^2 \rangle = \langle [\Delta E_0]^2 \rangle = C_v k_B T^2.
\] (8)

For a vibrator with one degree of freedom due to the energy equipartitioning \( C_v \simeq k_B \). Multiplying Eq. (5) by \( \Delta E_0 = \Delta E(0) \) and averaging over initial states we calculate the energy time correlation function (ETCF)
\[
\langle \Delta E(0)\Delta E(t) \rangle = C_v k_B T^2 e^{-\gamma t}.
\] (9)

Eq. (7) being averaged over initial states and in the long time limit allows one to determine the constant
\[
A = \gamma(\alpha + \gamma)k_B^2 T^2.
\] (10)

Let us introduce into consideration the deviation of the oscillator energy from its initial value during time \( t \)
\[
\delta E(t) = E(t) - E_0 = \Delta E(t) - \Delta E_0.
\] (11)

The evolution of its ensemble mean square deviation depends on the initial energy deviation
\[
\langle [\delta E(t)]^2 \rangle_0 = \langle [\Delta E(t)]^2 \rangle_0 - 2\Delta E_0 \langle \Delta E(t) \rangle_0 + (\Delta E_0)^2,
\]
and in accordance with Eq. (7) it can be written as
\[
\langle [\delta E(t)]^2 \rangle_0 = (\Delta E_0)^2(1 - e^{-\gamma t})^2 + \frac{A\alpha}{\gamma(\alpha^2 - \gamma^2)}(1 - e^{-2\gamma t}) - \frac{A}{\alpha^2 - \gamma^2}(1 + e^{-2\gamma t} - 2e^{-(\alpha + \gamma)t}).
\] (12)

The ensemble averaging over initial states yields the expression
\[
\langle [\delta E(t)]^2 \rangle = 2C_v k_B T^2[1 - e^{-\gamma t} - \frac{\gamma}{\alpha - \gamma}e^{-2\gamma t}(1 - e^{-(\alpha - \gamma)t})].
\] (13)

for the energy mean square fluctuations (EMSF). Its first order time derivative
\[
d\langle [\delta E(t)]^2 \rangle/dt = 2C_v k_B T^2[\gamma e^{-\gamma t} + \frac{2\gamma^2}{\alpha - \gamma}e^{-2\gamma t}(1 - \frac{\alpha + \gamma}{\alpha - \gamma}e^{-(\alpha - \gamma)t})].
\] (14)

is equal to zero at \( t = 0 \). The second order time derivative at the initial moment is equal to \( \gamma(\alpha + 2\gamma) \).

It is worthwhile to note that for white noise when Dirac’s \( \delta \)-function is used in Eq. (3) instead of the exponential function, the mean square deviation decay remains as given by Eq. (5) while the mean square deviation can be formally deduced from Eqs. (7), (12) and (13) in the limit \( \alpha \to \infty \) and with constant \( A \) given by Eq. (9). For example,
\[
\langle [\delta E(t)]^2 \rangle = 2C_v k_B T^2(1 - e^{-\gamma t}).
\] (15)

The right value of the first order time derivative of Eq. (15) at initial moment can be deduced from Eq. (14) if first the limit \( \alpha \to \infty \) is taken and then time \( t = 0 \) is considered. It results in \( 2C_v k_B T^2 \gamma \) instead of zero for the case when \( \alpha \) is arbitrary large but finite. In fact, the results are consistent because the second order time derivative is proportional to \( \alpha \) at \( t = 0 \).

### 3 Molecular dynamics simulation of the energy fluctuations

#### 3.1 The model and MD simulation procedure

In the MD simulations the classical equations of motion for a system of several hundreds of spherically
symmetric bath particles and a flexible diatomic are numerically integrated. The diatomic is represented by a harmonic oscillator with a gas phase frequency of $\nu = 188 \text{ cm}^{-1}$ that corresponds to the lowest vibrational frequency of azulene because just this molecule was extensively studied experimentally [11,12] and theoretically [14,17,18]. The interactions of the bath particles and between the bath particles and the diatomic atoms are described by nonlinear Lennard–Jones potential

$$\Phi_{\zeta}(r) = 4\varepsilon \left[\left(\frac{\sigma_{\zeta}}{r}\right)^{12} + \left(\frac{\sigma_{\zeta}}{r}\right)^{6}\right], \quad \zeta = u, v,$$

where $\sigma$ and $\varepsilon$ are size and energetic potential parameters. Subscripts $u$ and $v$ are used for solute–solvent and solvent–solvent interactions, respectively.

The particular values $\varepsilon_v/k_B = 283.2 \text{ K}$, $\varepsilon_u/k_B = 480 \text{ K}$, $\sigma_v = 0.47 \text{ nm}$, $\sigma_u = 0.52 \text{ nm}$ are used. $R_c = 0.14 \text{ nm}$ and $0.2 \text{ nm}$ are two values of the diatomic equilibrium bond lengths (internuclear distances) considered. Atomic masses of $m_v = 44 \text{ kg/kmol}$ and $m_u = 64 \text{ kg/kmol}$ at a dimensionless solvent density of $\rho = \sigma_v^3 N/V = 0.6$ at slightly supercritical temperature $k_B T/\varepsilon_v = 1.32$ are chosen to mimic the azulene–propane system. Here $N$ and $V$ are number of particles and cubic simulation box volume, respectively. Periodic boundary conditions are used.

The MD simulations were performed in a microcanonical (NEV) ensemble of 256 or 500 particles employing the leap-frog Verlet algorithm [24]. According to Ref. [25] we used modified Lennard–Jones potentials that keep the forces continuous at the cutoff distance $R_c$

$$\Phi_{\zeta}^{(c)}(r) = \{\Phi_{\zeta}(r) - \Phi_{\zeta}(R_c) + 12\varepsilon [2\left(\frac{\sigma_{\zeta}}{R_c}\right)^{12} - \left(\frac{\sigma_{\zeta}}{R_c}\right)^{6} - \frac{r}{R_c}]\theta(R_c - r),$$

where $\theta(x)$ is the Heaviside step function and $R_c$ in our calculations was half the box length. This cutoff scheme efficiently reduces high frequency artefacts in the power spectrum of the TCFs [26].

The integration step size was 4 fs and the trajectory length was $2^{22}$ time steps after an equilibration period of 40 ps. At each time step the power of forces exerted on the diatomic vibrational coordinate, the diatomic total and the system kinetic energy were recorded. The solvent temperature was calculated from the system mean kinetic energy.

A special rescaling procedure was developed and used before the equilibration period to insure the solvent temperature to be close to the desired value $1.32\varepsilon_v/k_B$. This procedure is based on the caloric equation of state $E_t = E_t(T, \rho)$. The solvent density $\rho$ is determined by the number of particles and the simulation box volume. Trail simulations during $10 \text{ ps}$ at three different system total energies $E_t$ (that remains constant during the simulation in NEV ensemble used) were performed to estimate the respective temperatures. The initial energies where chosen to get temperatures around the desired value. The final energy correction was calculated by parabolic interpolation of the equation of state and put into the kinetic part of the system energy. All the energy corrections were done by rescaling particle velocities. After the procedure is fulfilled the deviation from the desired value of the mean temperature calculated over a long equilibrium trajectory was typically within one per cent.

Nonequilibrium MD simulations were performed as well. The ensemble of nonequilibrium trajectories was created extracting the initial system states separated by time intervals of $10 \text{ ps}$ from a long equilibrium trajectory. For each of the initial states an additional kinetic energy was put into the vibrational degree of freedom by changing solute atom velocities preserving its center of mass velocity unchanged. Each trajectory was propagated in time with the leap-frog algorithm mentioned above. Vibrator energy was recorded at each time step and averaged over the ensemble of trajectories.
3.2 Simulation results and discussion

In order to determine energy time correlation functions (ETCFs) by means of the Fast Fourier Transform (FFT) algorithm time series were divided into overlapping segments of 8192 time steps (neighboring segments are shifted by 1024 time steps), and the resulting ETCF was averaged. The mean square energy fluctuations (at \( t = 0 \)) were also calculated. The oscillator heat capacity as estimated from the mean square energy fluctuations was a few per cent lower than the expected value \( k_B \) and may signify that the solute–bath interaction lowers the oscillator heat capacity.

For evaluating the mean square energy fluctuations the trajectories were cut into pieces and the appropriate time series (the squared difference of the current and initial oscillator energy) where calculated inside of each of the pieces and averaged over them. The lengths and numbers of the pieces were 40 ps and 400 for \( R_e = 0.14 \) nm and 20 ps and 800 for \( R_e = 0.20 \) nm, respectively. Dimensionless temperature \( k_B T/\epsilon_v \) was calculated to yield 1.32 for the former and 1.29 for the latter case.

In Fig. 1 the time correlation functions of energy deviation are shown. Their decays can be roughly approximated by monoexponentials with time constants \( \tau = 6.1 \) ps and 6.8 ps for \( R_e = 0.14 \) nm and 0.2 nm, respectively. There are small drops (around 10 per cent) on initial subpicosecond time space on both curves. The time constants do not change noticeable if this time space is omitted.

On the other hand, the energy mean square fluctuations (Figs. 2 and 3) follow neither Eq. (13) nor Eq. (15) because on the time scale of the figures they are not equal to zero at \( t = 0 \). However, on a shorter time scale it is evident (see the inserts in Figs. 2 and 3) that the EMSFs can be approximated by Eq. (13). It means that the memory effects are important for the description of the dynamics of energy relaxation on the short time scale of the order of 0.1 ps. This is just the time scale of a collision. It was shown earlier that collisions of the solute with solvent molecules are well resolved even at solvent densities as high as 0.8. The characteristic times of the binary collisions are also of the order of 0.1 ps [14].

Thus, VER has to be considered as a two-stage process:

(i) At short times during a collision, strong autocorrelation (memory) of the solute–solvent intermolecular power source exists. The interaction is strong and the effective friction coefficient is large that results in significant rise of the energy mean square deviation on this short time that can be

![Energy time correlation function versus time at \( R_e = 0.14 \) nm (a) and 0.20 nm (b). Dashed lines represent exponential fitting curves with time constants \( \tau = 6.1 \) ps (a) and 6.8 ps (b).]
roughly represented by Eq. (13). However, during a collision complete relaxation of the solute vibrational energy is impossible, and the quantity $Q_0$ should be used in front of square brackets instead of heat capacity and squared temperature. $Q_0$ is approximately equal to 0.45 and 0.36 (in units of $\varepsilon^2$) for $R_e=0.14$ nm and 0.2 nm, respectively. The time constants for fitting the short time dependence of EMSFs are $\gamma^{-1}=67$ fs, $\alpha^{-1}=44$ fs for both values of the internuclear distance.

(ii) On the longer time scale correlation between different collisions does not exist and the VER process becomes a stochastic process without memory that can be described by the expression like Eq. (15)

$$\langle [\delta E(t)]^2 \rangle = Q_1 + (2C_v k_B T^2 - Q_1)(1-e^{-\gamma_1 t}).$$  \hspace{1cm} (18)

This expression yields nonzero initial value and has a right asymptotic in the long time limit. However, estimated values of $Q_1$ (0.3 and 0.2) differ from the $Q_0$ values given above. The relaxation time $\tau_1 = \gamma_1^{-1} = 8.8$ ps for both values of $R_e$. The vibrator heat capacity as estimated from the long time asymptotic of EMSFs is close to $k_B$.

The difference in $Q$ values can be easily explained by overlapping the processes on the short and long time intervals while the relaxation times difference cannot be explained in such a way because the estimations of $\tau$ do not change when the reduction of ETCFs during short initial time range is omitted. The latter difference can be a result of poor statistics or more adequate stochastic equation has to be used instead of Eq. (1).

In Figs. 2 and 3 at times above 10 ps the approaching of the EMSFs to their equilibrium values seems to become slower as compared to Eq. (16) indicating another time scale can come into play in the VER process. This statement, however, has to be checked with better statistics.

The inserts in Figs. 2 and 3 demonstrate one more peculiarity of the short time behavior of the EMSFs. Strong oscillations are superimposed over the relaxation curves. This peculiarity is closely connected with the dynamics of the solute–solvent interaction.
energy exchange. The period of the oscillations is about 0.17 ps close to the vibrational period of 0.177 ps of the isolated solute vibrator frequency of 188 cm$^{-1}$. This blue shift of the oscillator frequency can be explained by the mean force potential that is created by bath molecules.

It was demonstrated [27] that the solute–solvent energy exchange strongly depends on the specific oscillator phase (bond elongations or contractions) for direct energy transfer and for rotation-vibration coupling as well. Just this dependence is manifested in the short time behavior of the EMSFs until the dephasing of vibrations due to solute–solvent interactions washes out the oscillations. This observation can be used for elaborating a more precise stochastic model of VER in fluids.

The results of nonequilibrium simulations are shown in Fig. 4 for the same solvent density and temperature as in the case of the equilibrium simulations. The solute internuclear distance was equal to 0.2 nm. The initial solute vibrational energy was taken five times higher than its thermal equilibrium value and the simulation results were averaged over 100 trajectories. The mean energy deviation decay can be well fitted by an exponential dependence with a time constant of 9.9 ps, which is in a good agreement with 8.8 ps from EMSF evolution. However, both these values are well above of the time constant 6.8 ps characterizing the equilibrium ETCF decay.

The simulation results show that the bond length variation slightly changes numerical values of some characteristics but all the main features of the curves remain unchanged. The length of the time range for investigating the mean squared energy fluctuations at the parameters considered have to be 40 ps ($10^4$ time steps) at least. The statistics over several hundred samples provides a qualitative description of the energy diffusional behavior but even 800 samples are not sufficient to derive firm conclusions about quantitative stochastic characteristics of the solute energy fluctuations.

![FIG. 4. Nonequilibrium simulation results for mean energy decay. The smooth white curve is an exponential fit with a time constant of $\tau=9.9$ ps.](image)

### 4 Conclusions

The generalized Langevin equation for energy fluctuations with stochastic power source that takes into account memory effects is considered. It is shown that the mean square energy fluctuations side by side with the energy relaxation can be used for the analysis of the solute–solvent energy exchange.

The analysis reveals at least two considerably different time scales of the energy exchange. At short times on the order of the collision time strong effective friction and significant memory effects dominate. At longer times friction is much lower and memory effects are of no importance.

The Langevin equation that takes into account memory effects only via characteristics of the stochastic power source allows for qualitative description of the energy fluctuations. Thus, a more general Langevin equation with the mean potential term and memory effects included into the dissipation term is in order for proper consideration of vibrational energy relaxation. Again, for MD equilibrium and nonequilibrium simulations better statistics is necessary to make more definite conclusions.
about the validity and interpretation of expressions of the stochastic analysis. This work is in progress now.

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