Anharmonic quantum contribution to vibrational dephasing

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Abstract

Based on a quantum Langevin equation and its corresponding Hamiltonian within a c-number formalism we calculate the vibrational dephasing rate of a cubic oscillator. It is shown that leading order quantum correction due to anharmonicity of the potential makes a significant contribution to the rate and the frequency shift. We compare our theoretical estimates with those obtained from experiments for small diatomics $N_2$, $O_2$ and $CO$.

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I. INTRODUCTION

A molecule in a liquid undergoes random frequency fluctuations due to the stochastic forces imparted by the surrounding medium. The correlation between this frequency fluctuations results in vibrational dephasing. The problem has received wide attention both from theoretical and experimental point of view over the last couple of decades. Several approaches to understand the basic nature of vibrational dephasing have been made. These include notably binary collision theory\(^1\) in which fluctuations are taken into account in terms of collisional events, hydrodynamic model\(^2,3,4,5\) relating random force and shear viscosity of the liquid, Hamiltonian theory\(^6\) in terms of normal mode analysis and numerical simulations\(^7,8,9,10,11\) using various molecular potentials. A key element of these formulations is the realization that vibrational dephasing owes its origin to cubic anharmonicity of the vibrational potential. In the present paper we attempt to explore further this issue within a quantum mechanical content.

A good number of approaches to vibrational dephasing make use of generalized Langevin equation that governs the dynamics of the system by an infinite number of harmonic oscillators coupled linearly to the system. Very recently based on a coherent state representation of noise operator and a positive definite Wigner canonical thermal distribution\(^19\) of bath oscillators a c-number quantum Langevin equation\(^20,21,22,23,24,25,26\) in the context of rate theory and stochastic processes has been proposed. An important offshoot of this formulation is that it takes care of quantum correction due to nonlinearity of the system potential order by order. It would thus seem that one should be able to analyze the vibrational dephasing rate quantum mechanically for arbitrary noise correlation and temperature and explore the role of this quantum correction to anharmonicity. This is the main purpose of this paper. In what follows we construct a c-number Hamiltonian within a normal mode description and estimate the dephasing rate by calculating the effective correlation between the relevant c-number co-ordinates of anharmonic origin. Since for a small diatomic molecule like N\(_2\), the fundamental vibrational frequency \(\omega_0\) is so high (2326 cm\(^{-1}\)) that the ratio \(\hbar\omega_0/kT\) is as large as 43.52 even at, say, 77 \(^0\)K, it is imperative that quantum nature of the oscillator molecule is significant in estimating the dephasing rate in the harmonic as well as in the anharmonic regime. With this end in view we examine the vibrational dephasing rate to estimate the anharmonic quantum correction to this rate and its variation with temperature.
away from critical or triple point for three widely studied diatomics \( N_2, O_2 \) and \( CO \) to allow ourselves a fair comparison with experiments \(^{12,13,14,15,16,17,18} \).

The outlay of the paper is as follows: In Sec.II we introduce the quantum Langevin equation and its Hamiltonian counterpart within a c-number normal mode description. Since the cubic nonlinearity gives rise to a leading order contribution to dephasing rate we estimate the quantum vibrational dephasing rate for a cubic oscillator in Sec.III. The quantum corrections due to nonlinearity of the system potential is calculated explicitly in Sec.IV. Sec.V is devoted to the results obtained theoretically for three diatomics \( N_2, O_2 \) and \( CO \) which are compared with experiments. The paper is concluded in Sec. VI.

II. C-NUMBER QUANTUM Langevin EQUATION AND NORMAL MODE TRANSFORMATION

We consider a particle of mass \( \mu \) coupled to a medium comprised of a set of harmonic oscillators with frequency \( \omega_i \). This is described by the following Hamiltonian:\(^6\)

\[
H = \frac{\hat{p}^2}{2\mu} + V(\hat{q}) + \sum_{i=1}^{N} \left\{ \frac{\hat{p}_i^2}{2m_i} + \frac{m_i}{2}(\omega_i\hat{x}_i + \frac{c_i}{m_i\omega_i}\hat{q})^2 \right\} \tag{2.1}
\]

Here \( \hat{q} \) and \( \hat{p} \) are co-ordinate and momentum operators of the particle and the set \( \{\hat{x}_i, \hat{p}_i\} \) is the set of co-ordinate and momentum operators for the reservoir oscillators of mass \( m_i \) coupled linearly to the system through their coupling coefficients \( c_i \). The potential \( V(\hat{q}) \) is due to the external force field for the Brownian particle. The co-ordinate and momentum operators follow the usual commutation relations \([\hat{q}, \hat{p}] = i\hbar\) and \([\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}\).

Eliminating the reservoir degrees of freedom in the usual way we obtain the operator Langevin equation for the particle,

\[
\mu \ddot{\hat{q}}(t) + \mu \int_0^t dt' \gamma(t-t')\dot{\hat{q}}(t') + V'(\hat{q}) = \hat{F}(t) \tag{2.2}
\]

where the noise operator \( \hat{F}(t) \) and the memory kernel \( \gamma(t) \) are given by

\[
\hat{F}(t) = -\sum_j \left\{ \frac{m_j\omega_j^2}{c_j} \hat{x}_j(0) + \hat{q}(0) \right\} \frac{c_j^2}{m_j\omega_j^2} \cos \omega_j t + \frac{c_j}{m_j\omega_j} \hat{p}_j(0) \sin \omega_j t \tag{2.3}
\]
\[ \gamma(t) = \sum_{j=1}^{N} \frac{c_j^2}{m_j \omega_j^2} \cos \omega_j t, \quad (2.4) \]

The Eq. (2.2) is the well known exact quantized operator Langevin equation for which the noise properties of \( \hat{F}(t) \) can be derived by using a suitable initial canonical distribution of the bath co-ordinate and momentum operators at \( t = 0 \) as follows;

\[ \langle \hat{F}(t) \rangle_{QS} = 0 \quad (2.5) \]

\[ \frac{1}{2} \{ \langle \hat{F}(t) \hat{F}(t') \rangle_{QS} + \langle \hat{F}(t') \hat{F}(t) \rangle_{QS} \} = \frac{1}{2} \sum_{j=1}^{N} \frac{c_j^2}{m_j \omega_j^2} \hbar \omega_j \left( \coth \frac{\hbar \omega_j}{2k_BT} \right) \cos \omega_j (t - t') \quad (2.6) \]

where \( \langle ... \rangle_{QS} \) refers to quantum statistical average on bath degrees of freedom and is defined as

\[ \langle \hat{O} \rangle_{QS} = \frac{\text{Tr} \hat{O} \exp(-\hat{H}_{\text{bath}}/k_BT)}{\text{Tr} \exp(-\hat{H}_{\text{bath}}/k_BT)} \quad (2.7) \]

for any operator \( \hat{O} = \{ (m_j \omega_j^2/c_j) \hat{x}_j + \hat{q}_j \}, \{ \hat{p}_j \} \) where \( \hat{H}_{\text{bath}}(\sum_{i=1}^{N} \left( \frac{\hat{p}_i^2}{2m_i} + \frac{m_i}{2} \omega_i \hat{x}_i + \frac{\alpha_i}{m_i \omega_i} \hat{q}_i^2 \right) ) \) at \( t = 0 \). By Trace we mean the usual quantum statistical average. Eq. (2.6) is the fluctuation-dissipation relation with the noise operators ordered appropriately in the quantum mechanical sense.

To construct a c-number Langevin equation\textsuperscript{20,21,22,23,24,25,26} we proceed from Eq. (2.2). We first carry out the quantum mechanical average of Eq. (2.2)

\[ \mu \langle \ddot{\hat{q}}(t) \rangle + \mu \int_0^t dt' \gamma(t - t') \langle \dot{\hat{q}}(t') \rangle + \langle V' \dot{\hat{q}} \rangle = \langle \hat{F}(t) \rangle \quad (2.8) \]

where the quantum mechanical average \( \langle ... \rangle \) is taken over the initial product separable quantum states of the particle and the bath oscillators at \( t = 0 \), \( \{ |\phi \rangle \{ |\alpha_1 \rangle |\alpha_2 \rangle \ldots |\alpha_N \rangle \} \). Here \( |\phi \rangle \) denotes any arbitrary initial state of the particle and \( |\alpha_i \rangle \) corresponds to the initial coherent state of the \( i \)-th bath oscillator. \( |\alpha_i \rangle \) is given by \( |\alpha_i \rangle = \exp(-|\alpha_i|^2/2) \sum_{n_i=0}^{\infty} (\alpha_i^{n_i}/\sqrt{n_i}) |n_i \rangle, \alpha_i \) being expressed in terms of the mean values of the shifted co-ordinate and momentum of the \( i \)-th oscillator, \( \{ (m_i \omega_i^2/c_i) \langle \hat{x}_i(0) \rangle + \langle \hat{q}(0) \rangle \} = \sqrt{\hbar/2m_i \omega_i (\alpha_i + \alpha_i^*) } \) and \( \langle \hat{p}_i(0) \rangle = i \sqrt{\hbar m_i \omega_i /2} (\alpha_i^* - \alpha_i) \), respectively. It is important to note...
that $\langle \hat{F}(t) \rangle$ of Eq. (2.8) is a classical-like noise term which, in general, is a non-zero number because of the quantum mechanical averaging and is given by $(\langle \hat{F}(t) \rangle \equiv f(t))$;

$$f(t) = -\sum_j \left[ \left\{ \frac{m_j \omega_j^2}{c_j} (\hat{x}_j(0)) + \langle \hat{q}(0) \rangle \right\} \frac{c_j^2}{m_j \omega_j^2} \cos \omega_j t + \frac{c_j}{m_j \omega_j} (\hat{p}_j(0)) \sin \omega_j t \right]$$ (2.9)

It is convenient to rewrite the c-number equation (2.8) as follows;

$$\mu\langle \ddot{\hat{q}}(t) \rangle + \mu \int_0^t dt' \gamma(t-t') \langle \dot{\hat{q}}(t') \rangle + \langle V'(\hat{q}) \rangle = f(t)$$ (2.10)

To realize $f(t)$ as an effective c-number noise we now introduce the ansatz\textsuperscript{19,20,21,22,23,24,25,26} that the momenta $\langle \hat{p}_j(0) \rangle$ and the shifted co-ordinates \{$(m_j \omega_j^2/c_j) \langle \hat{x}_j(0) \rangle + \langle \hat{q}(0) \rangle$, $\hat{p}_j$\} of the bath oscillators are distributed according to a canonical distribution of Gaussian form as

$$\mathcal{P}_j = N \exp \left\{ -\frac{[\langle \hat{p}_j(0) \rangle^2 + \frac{c_j^2}{\omega_j^2} (\frac{m_j \omega_j^2}{c_j} \langle \hat{x}_j(0) \rangle + \langle \hat{q}(0) \rangle)^2]}{2 \hbar m_j \omega_j (\bar{n}_j(\omega_j) + \frac{1}{2})} \right\}$$ (2.11)

so that for any function of the quantum mechanical mean values of the bath operator $O_j(\langle \hat{p}_j(0) \rangle, ((m_j \omega_j^2/c_j) \langle \hat{x}_j(0) \rangle + \langle \hat{q}(0) \rangle))$ the statistical average $\langle \ldots \rangle_S$ is

$$\langle O_j \rangle_S = \int O_j \mathcal{P}_j d\langle \hat{p}_j(0) \rangle d\{((m_j \omega_j^2/c_j) \langle \hat{x}_j(0) \rangle + \langle \hat{q}(0) \rangle) \}.$$ (2.12)

Here $\bar{n}_j$ indicates the average thermal photon number of the $j$-th oscillator at temperature $T$ and $\bar{n}_j(\omega_j) = 1/[\exp (\hbar \omega_j/k_B T) - 1]$ and $N$ is the normalization constant.

The distribution (2.11) and the definition of statistical average (2.12) imply that $f(t)$ must satisfy

$$\langle f(t) \rangle_S = 0$$ (2.13)

and

$$\langle f(t)f(t') \rangle_S = \frac{1}{2} \sum_j \frac{c_j^2}{m_j \omega_j^2} \hbar \omega_j \left( \coth \frac{\hbar \omega_j}{2 k_B T} \right) \cos \omega_j (t - t')$$ (2.14)

That is, c-number noise $f(t)$ is such that it is zero-centered and satisfies the standard fluctuation-dissipation relation (FDR) as expressed in Eq. (2.6). It is important to emphasize
that the ansatz (2.11) is a canonical thermal Wigner distribution\textsuperscript{19} for a shifted harmonic oscillator which remains always a positive definite function. A special advantage of using this distribution is that it remains valid as pure state non-singular distribution function at $T = 0$. Furthermore, this procedure allows us to bypass the operator ordering prescription of Eq.(2.6) for deriving the noise properties of the bath in terms of fluctuation-dissipation relation and to identify $f(t)$ as a classical looking noise with quantum mechanical content. The procedure has been used by us in several recent contexts\textsuperscript{20,21,22,23,24,25,26}.

We now return to Eq.(2.10) to add the force term $V'(\langle \hat{q} \rangle)$ on both sides of Eq.(2.10) and rearrange it to obtain

\begin{align}
\mu \dot{q} &= p \tag{2.15} \\
\dot{p} &= -\int_{0}^{t} dt' \gamma(t - t') p(t') - V'(q) + f(t) + Q(t) \tag{2.16}
\end{align}

where we put $\langle \dot{q}(t) \rangle = q(t)$ and $\langle \dot{p}(t) \rangle = p(t)$ for notational convenience and

$$Q(t) = V'(\langle \hat{q} \rangle) - \langle V'(\hat{q}) \rangle$$

(2.17)

represents the quantum correction due to the system degrees of freedom. Eq.(2.16) offers a simple interpretation. This implies that the quantum Langevin equation is governed by a $c$-number quantum noise $f(t)$ originating from the heat bath characterized by the properties (2.13) and (2.14) and a quantum fluctuation term $Q(t)$ characteristic of the non-linearity of the potential.

Referring to the quantum nature of the system in the Heisenberg picture, one may write.

$$\hat{q}(t) = q + \delta \hat{q} \tag{2.18}$$
$$\hat{p}(t) = p + \delta \hat{p} \tag{2.19}$$

where $\langle \hat{q} \rangle(= q)$ and $\langle \hat{p} \rangle(= p)$ are the quantum-mechanical averages and $\delta \hat{q}$, $\delta \hat{p}$ are the operators. By construction $\langle \delta \hat{q} \rangle$ and $\langle \delta \hat{p} \rangle$ are zero and $[\delta \hat{q}, \delta \hat{p}] = i\hbar$. Using Eqs.(2.18) and (2.19) in $\langle V'(\hat{q}) \rangle$ and a Taylor series expansion around $\langle \hat{q} \rangle$ it is possible to express $Q(t)$ as

$$Q(t) = -\sum_{n \geq 2} \frac{1}{n!} V^{(n+1)}(q) \langle \delta \hat{q}^n(t) \rangle$$

(2.20)
Here $V^{(n)}(q)$ is the n-th derivative of the potential $V(q)$. For example, the second order $Q(t)$ is given by $Q(t) = -\frac{1}{2}V''(q)\langle \delta q^2 \rangle$. The calculation of $Q(t)$ therefore rests on quantum correction terms, $\langle \delta q^n(t) \rangle (= B_n(t))$ which are determined by solving the quantum correction equations as discussed in the Sec.IV.

The c-number Hamiltonian corresponding to Langevin equation (2.15, 2.16) is given by

$$H = \frac{p^2}{2\mu} + \left[ V(q) + \sum_{n \geq 2} \frac{1}{n!} V^{(n)}(q)B_n(t) \right] + \sum_{i=1}^{N} \left\{ \frac{p_i^2}{2m_i} + \frac{m_i}{2}\left(\omega_1^2x_i + \frac{c_i}{m_i\omega_1}q\right)^2 \right\} \quad (2.21)$$

Note that the above Hamiltonian is different from our starting Hamiltonian operator (2.1) because of the c-number nature of (2.21). $\{x_i, p_i\}$ are the quantum mean values of the co-ordinate and the momentum operators of the bath oscillators.

To characterize the properties of the bath we define, as usual, the spectral density function as

$$J(\omega) = \frac{\pi}{2\mu} \sum_{i=1}^{N} \frac{c_i^2}{m_i\omega_i} \delta(\omega - \omega_i) \quad (2.22)$$

Splitting the potential into a linear and nonlinear part as

$$V(q) = \frac{1}{2}\mu\omega_0^2q^2 + V_1(q) \quad (2.23)$$

where $V_1(q)$ is the nonlinear part of the classical potential $V(q)$ we express, using (2.23), the quantum correction term as

$$\sum_{n \geq 2} \frac{1}{n!} V^{(n)}(q)B_n(t) = \frac{1}{2}\mu B_2(t)\omega_0^2 + V_2(q) \quad (2.24)$$

$$V_2(q) = \sum_{n \geq 2} \frac{1}{n!} B_n(t)V_1^{(n)}(q)$$

Therefore the c-number Hamiltonian (Eq. 2.21) can be written as

$$H = H_0 + V_N(q) \quad (2.25)$$

where, $H_0$, the harmonic part of the Hamiltonian is given by

$$H_0 = \frac{p^2}{2\mu} + \frac{1}{2}\mu\omega_0^2q^2 + \frac{1}{2}\mu B_2\omega_0^2 + \sum_{i=1}^{N} \left\{ \frac{p_i^2}{2m_i} + \frac{m_i}{2}\left(\omega_1^2x_i + \frac{c_i}{m_i\omega_1}q\right)^2 \right\} \quad (2.26)$$
and $V_N(q)$ is given by

$$V_N(q) = V_1(q) + V_2(q) \quad \text{(2.27)}$$

$V_2(q)$ is the quantum correction term due to nonlinear part of the system potential. We define the mass weighted co-ordinates as

$$q' = \sqrt{\mu} q \quad \text{and} \quad x'_j = \sqrt{m_j} x_j \quad \text{(2.28)}$$

Diagonalizing the force constant matrix $T$ of the Hamiltonian (Eq.2.26) as

$$U T = \lambda^2 U \quad \text{(2.29)}$$

where $U$ provides the transformation from old co-ordinates to the normal co-ordinates.\(^6,29\)

\[
\begin{pmatrix}
\rho \\
y_1 \\
y_2 \\
\vdots \\
y_N
\end{pmatrix}
= U
\begin{pmatrix}
q' \\
x'_1 \\
x'_2 \\
\vdots \\
x'_N
\end{pmatrix}
\quad \text{(2.30)}
\]

Here $\rho$ and $y_i$ are normal co-ordinates corresponding to system and bath modes respectively.

The normal mode Hamiltonian for the harmonic part $H_0$ is then given by\(^8\),

$$H_{NM} = \frac{1}{2} \rho^2 + \frac{1}{2} \lambda_0^2 \rho^2 + \sum_{j=1}^{N} \left[ \frac{1}{2} y_j^2 + \frac{1}{2} \lambda_j^2 y_j^2 \right] \quad \text{(2.31)}$$

The eigenvalues $\lambda_0^2$ and $\lambda_j^2$ are expressible in terms of the coupling constants of the system and the bath implicitly as follows:

$$\lambda_0^2 = \omega_0^2/ \left[ 1 - \frac{1}{\mu} \sum_{j=1}^{N} \frac{c_j^2}{m_j \omega_j^2 (\lambda_0^2 - \omega_j^2)} \right] \quad \text{(2.32)}$$

$$\lambda_i^2 = \omega_0^2 \left[ 1 - \frac{1}{\mu} \sum_{j=1}^{N} \frac{c_j^2}{m_j \omega_j^2 (\lambda_i^2 - \omega_j^2)} \right], \quad i = 1, 2, \ldots N \quad \text{(2.33)}$$
where (2.32) and (2.33) correspond to normal mode frequencies of the system and \(i\)-th bath oscillator respectively.

The transformation (2.30) explicitly implies,

\[
q' = u_{00} \rho + \sum_{j=1}^{N} u_{j0} y_j
\]  

(2.34)

where the matrix elements \(u_{00}\) and \(u_{j0}\) can be expressed as

\[
u_{00}^2 = \frac{1}{1 + \frac{1}{\mu} \sum_{j=1}^{N} \frac{c_j^2}{m_j (\lambda_0^2 - \omega_j^2)^2}}
\]  

(2.35)

\[
u_{i0}^2 = \frac{1}{1 + \frac{1}{\mu} \sum_{j=1}^{N} \frac{c_j^2}{m_j (\lambda_i^2 - \omega_j^2)^2}} , \quad i = 1, 2 \ldots N
\]  

(2.36)

For the present problem of dephasing it is significant to consider the coupling between the system and the bath modes to be weak. One can make use of the perturbation technique and \(\lambda_0^2\) and \(\lambda_i^2\) are then expressible in simple terms as follows,

\[
\lambda_0^2 = \omega_0^2 \left[1 - \frac{1}{\mu} \sum_{j=1}^{N} \frac{c_j^2}{m_j \omega_j^2 (\omega_j^2 - \omega_0^2)} \right] + O(c_j^4)
\]

\[
\omega_i^2 = \omega_j^2 \left[1 + \frac{c_j^2}{\mu m_j \omega_j^2 (\omega_j^2 - \omega_0^2)} \right] + O(c_j^4) , \quad j = 1, 2 \ldots N
\]

\[
u_{j0} = -u_{0j} = \frac{c_j}{\sqrt{\mu m_j (\omega_j^2 - \omega_0^2)}} + O(c_j^2) , \quad j = 1, 2 \ldots N
\]

\[
u_{ii} = 0 + O(c_j^2) , \quad ij \neq 0
\]

III. QUANTUM VIBRATIONAL DEPHASING RATE FOR A CUBIC OSCILLATOR

It has already been established\(^2,3,4\) that harmonic oscillator model is not sufficient for a quantitative description of vibrational dephasing rate. The essential paradigm for the theory that has been used over the decades involves cubic nonlinearity so that the potential
assumes the following form,

\[ V(q) = \frac{1}{2} \mu \omega_0^2 q^2 + \frac{1}{6} f q^3 \]  

(3.1)

Here \( f \) is a constant due to cubic nonlinearity. With Eq. (3.1) the full Hamiltonian \( H \) in normal co-ordinate is given by

\[ H = H_{NM} + k_{111}(u_{00} \rho + \sum_{j=1}^{N} u_{j0} y_j)^3 + 3\mu B_2 u_{00}^2 k_{111}(u_{00} \rho + \sum_{j=1}^{N} u_{j0} y_j) + \mu^{3/2} B_3 u_{00}^3 k_{111} \]  

(3.2)

where we have used Oxtoby’s notation, \( k_{111} = f/6\mu^{3/2} \) and relations (2.27) and (2.28). Here the first term denotes the normal mode Hamiltonian for the harmonic potential and the second term corresponds to classical nonlinear part of the potential. In addition to a constant shift of quantum origin third term signifies the quantum corrections to system normal mode where nonlinearity and quantum effects are entangled. In what follows we show that this term provides a substantial contribution to the vibrational dephasing rate.

The anharmonicity in the potential shifts the minimum and the frequency of the system normal mode so that by applying the usual condition

\[ \left( \frac{\partial H}{\partial \rho} \right)_{\rho_e} = 0 \]  

(3.3)

to obtain the instantaneous minimum of the potential, \( \rho_e \), we have

\[ \rho_e = \frac{1}{6k_{111} u_{00}^3} \left[ - (\lambda_0^2 + 6k_{111} u_{00}^2 \sum_{j=1}^{N} u_{j0} y_j) + (\lambda_0^4 + 12\lambda_0^2 k_{111} u_{00}^2 \sum_{j=1}^{N} u_{j0} y_j - 36\mu B_2 u_{00}^6 k_{111}^{1/2}) \right] \]  

(3.4)

The instantaneous frequency is given by

\[ \lambda_0(t) = \left( \frac{\partial^2 H}{\partial \rho^2} \right)_{\rho_e}^{1/2} \]

\[ = \lambda_0 \left[ 1 + \frac{12 u_{00}^2 k_{111}}{\lambda_0^2} \sum_{j=1}^{N} u_{j0} y_j - \frac{36 \mu B_2(t) u_{00}^6 k_{111}^{1/2}}{\lambda_0^4} \right]^{1/4} \]

\[ \approx \lambda_0 \left[ 1 + \frac{3 k_{111}}{\lambda_0^2} \sum_{j=1}^{N} u_{j0} y_j - \frac{9 \mu B_2(t) k_{111}^2}{\lambda_0^4} \right] \]  

(3.5)
where we have used \( u_{00} \) in the leading order. The instantaneous frequency shift is therefore,

\[
\Delta \omega(t) = \lambda_0(t) - \lambda_0 = \frac{3k_{111}}{\lambda_0} \sum_{j=1}^{N} u_{j0} y_j - \frac{9 \mu B_2(t) k_{111}^2}{\lambda_0^3}
\]  

(3.6)

In the weak coupling limit the dephasing rate is expressed as,

\[
\kappa_{\text{dep}} = \int_0^\infty \langle \Delta \omega(t) \Delta \omega(0) \rangle \, dt
\]

(3.7)

where the averaging is carried out over the thermally distributed bath modes

\[
\langle \Delta \omega(t) \Delta \omega(0) \rangle = \frac{9k_{111}^2}{\lambda_0^2} \sum_{j=1}^{N} \frac{u_{j0}^2}{\lambda_j^2} \left[ \frac{1}{2} \hbar \lambda_j \coth \left( \frac{\hbar \lambda_j}{2k_B T} \right) \right] \cos(\lambda_j t) + \frac{81 \mu^2 k_{111}^4 B_2(0) \lambda_0^6}{\lambda_0^6} \int_0^\infty dt \, B_2(t)
\]

(3.8)

Here we have used the relations for the thermalized bath modes

\[
\langle y_i(0) \rangle_S = \langle \dot{y}_i(0) \rangle_S = \langle y_i(0) \dot{y}_i(0) \rangle_S = 0
\]

\[
\langle \dot{y}_i(0)^2 \rangle_S = \lambda_i^2 \langle y_i(0)^2 \rangle_S = \frac{1}{2} \hbar \lambda_i \coth \left( \frac{\hbar \lambda_i}{2k_B T} \right)
\]

(3.9)

The quantum dephasing rate is given by

\[
\kappa_{\text{dep}} = \frac{9k_{111}^2}{\lambda_0^2} \int_0^\infty dt \sum_{j=1}^{N} \frac{u_{j0}^2}{\lambda_j^2} \left[ \frac{1}{2} \hbar \lambda_j \coth \left( \frac{\hbar \lambda_j}{2k_B T} \right) \right] \cos(\lambda_j t) + \frac{81 \mu^2 k_{111}^4 B_2(0)}{\lambda_0^6} \int_0^\infty dt \, B_2(t)
\]

(3.10)

Using (2.37) for the expressions \( \lambda_0^2, \lambda_j^2 \) and \( u_{j0}^2 \) in (3.10) we obtain in the weak coupling regime

\[
\kappa_{\text{dep}} = \frac{9k_{111}^2}{\omega_0^2} \int_0^\infty dt \sum_{j=1}^{N} \frac{c_j^2}{\mu m_j \omega_j^2 (\omega_j^2 - \omega_0^2)} \left[ \frac{1}{2} \hbar \omega_j \coth \left( \frac{\hbar \omega_j}{2k_B T} \right) \right] \cos(\omega_j t) + \frac{81 \mu^2 k_{111}^4 B_2(0)}{\lambda_0^6} \int_0^\infty dt \, B_2(t)
\]

(3.11)

Use of Eq.(2.22) in the above expression and continuum limit results in
\[ \kappa_{\text{dep}} = \frac{18k_{111}^2}{\pi \omega_0^2} \int_0^\infty dt \int_0^\infty d\omega \frac{J(\omega)}{\omega} \frac{1}{(\omega^2 - \omega_0^2)^2} \left[ \frac{1}{2} \frac{\hbar \omega}{2k_B T} \coth \left( \frac{\hbar \omega}{2k_B T} \right) \right] \cos(\omega t) \]

\[ + \frac{81 \mu^2 k_{111}^4 B_2(0)}{\lambda_0^6} \int_0^\infty dt B_2(t) \]  

(3.12)

This is the general expression for quantum vibrational dephasing rate. The essential content of this formulae in addition to the usual first term obtained earlier by Levine et al.\textsuperscript{6} is the second term signifying the quantum contribution to dephasing rate arising out of the nonlinearity of the system potential. This term is independent of the quantum nature of the thermal bath. An evaluation of this term requires the explicit calculation of the integral over quantum correction term \( B_2(t) \) which we pursue in the next section. Keeping in view of the fact that \( J(\omega) \) does not involve a specific choice of form for density of bath modes, we find that the expression for the dephasing rate as derived above is fairly general.

The above method is based on the normal mode Hamiltonian of Pollak\textsuperscript{29} adopted to a c-number description. An analysis of pure dephasing of a nonlinear vibrational mode has been worked out earlier to calculate non-Markovian line shape by Georgievskii and Stuchebrukhov\textsuperscript{5} using normal mode Hamiltonian treated by thermodynamic Green’s function approach. While the basis of present calculation of dephasing rate is Eq.(3.7), the authors of Ref.5 have taken recourse to a different strategy to calculate the line shape. The differences in formulations and starting Hamiltonians (In Ref[5] a Leggett-Caldeira form of Hamiltonian, \textit{i.e.}, Eq.(2.1) without a counter term has also been employed) notwithstanding, the effect of a quantum contribution to dephasing width related to anharmonicity of the oscillator has been calculated in both Ref[5] and present analysis. The effect is due to the fact that the frequency of fundamental transition of a quantum nonlinear oscillator differs from harmonic frequency. To this end a continuation of the present analysis to calculate the associated frequency shift is instructive for comparison with those of others\textsuperscript{5,6}. For this we return to the expression (3.5) for instantaneous frequency \( \lambda_0(t) \), which after keeping terms upto \( k_{111}^2 \) may be written as

\[ \lambda_0(t) = \lambda_0 \left[ 1 + \frac{3k_{111}}{\lambda_0^2} \sum_{j=1}^N u_{j0} y_j(t) - \frac{27k_{111}^2}{2\lambda_0^4} \left( \sum_{j=1}^N u_{j0} y_j(t) \right)^2 - \frac{9\mu B_2(t)k_{111}^2}{\lambda_0^6} \right] \]

(3.13)

where we have put \( u_{00} \) to the leading order (unity). The time average frequency \( \overline{\lambda}_0 \) is
given by\(^6\)

\[
\overline{\lambda}_0 = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \lambda_0(t') \, dt'
\]  

(3.14)

Putting (3.13) in (3.14) we obtain

\[
\overline{\lambda}_0 = \lambda_0 \left[ 1 - \frac{27}{2} \frac{k_{111}^2}{\lambda_0^3} \sum_{j=1}^N \frac{u_{j0}^2}{\lambda_j^2} \left( \frac{1}{2} \frac{\hbar \lambda_j}{2k_BT} \right) \coth \left( \frac{\hbar \lambda_j}{2k_BT} \right) - \frac{9 \mu B_2 k_{111}^2}{\lambda_0^4} \right]
\]  

(3.15)

where we have used (3.9) and \( B_2 \) (= \( \omega_c \int_0^{1/\omega_c} B_2(t') \, dt' \), \( \omega_c \) being the cutoff frequency) is given by \( \frac{\hbar \omega_c \gamma}{8 \mu \omega_0^6} \) (the explicit form of \( B_2(t) \) is calculated in the next section). Furthermore with the replacement of \( u_{j0} \) using Eq.(2.37) and then using Eq.(2.22) in the continuum limit we obtain

\[
\overline{\lambda}_0 = \lambda_0 - \frac{27}{2} \frac{k_{111}^2 \hbar}{\pi \lambda_0^3 \omega_0} \int_0^{\omega_c} J(\omega) \coth \left( \frac{\hbar \omega}{2k_BT} \right) \, d\omega - \frac{9 k_{111}^2 \hbar \omega_c \gamma}{8 \lambda_0^3 \omega_0^3}
\]  

(3.16)

Since \( \lambda_0^2 \) is given by\(^6\),

\[
\lambda_0^2 = \omega_0^2 + \frac{2}{\pi} \int_0^{\omega_c} \frac{J(\omega)}{\omega} \, d\omega
\]  

(3.17)

one may use (4.9) to obtain

\[
\lambda_0 = \omega_0 \left[ 1 + \frac{\gamma \omega_c}{4 \pi \omega_0^2} \right]
\]  

(3.18)

The frequency shift \( \Delta \omega_0 \) is then derived from Eq.(3.16) and Eq.(3.18) as

\[
\Delta \omega_0 = \overline{\lambda}_0 - \omega_0 = \frac{\gamma \omega_c}{4 \pi \omega_0^2} - \frac{27}{8} \frac{\gamma k_{111}^2}{\pi \omega_0^5} \int_0^{\omega_c} \hbar \omega \coth \left( \frac{\hbar \omega}{2k_BT} \right) \, d\omega - \frac{9 k_{111}^2 \hbar \omega_c \gamma}{8 \omega_0^6}
\]  

(3.19)

It is important to note that while in addition to the first two terms corresponding to treatment of Levine, Shapiro and Pollak\(^6\) the last one refers to temperature independent anharmonic quantum contribution proportional to \( k_{111}^2 \) responsible to the frequency shift noted earlier in Ref.[5]. We mention in passing that the presence and absence of the counter term in the Hamiltonian may cause a significant difference in frequency shift with respect to direction towards blue or red region\(^6\). 

\[13\]
IV. CALCULATION OF THE QUANTUM CORRECTION DUE TO NONLINEARITY OF THE SYSTEM POTENTIAL

It has already been pointed out that a leading order quantum correction due to nonlinearity of the potential of the system provides an important contribution over and above the usual expression for dephasing rate. To calculate this term explicitly we now return to the operator equation (2.2) and use (2.18) and (2.19) to obtain

\[ \mu \delta \dot{q} = \delta \dot{p} \]  

\[ \delta \dot{p} + \int_0^t \gamma(t - t') \delta \dot{p}(t') \, dt' + V''(q) \delta \ddot{q} + \sum_{n \geq 2} \frac{1}{2} V^{(n+1)}(q) (\delta \dddot{q}^n - \langle \delta \dddot{q}^n \rangle) = \hat{F}(t) - f(t) \]  

We then perform a quantum mechanical averaging over bath states with \( \prod_{i=1}^N \{ |\alpha_i(0)\rangle \} \) to get rid of the term \( \hat{F}(t) - f(t) \). The Eqs. (4.1) and (4.2) along with (2.15) and (2.16) form the key element for calculation of the quantum mechanical correction. Considering the friction kernel \( \gamma(t) \) to be arbitrary (but decaying) we may calculate the leading order quantum correction for the harmonic mode for which higher derivatives of \( V(q) \) in (4.2) vanish. Now Eq. (4.2) becomes

\[ \delta \dot{p}(t) = - \int_0^t \gamma(t - t') \delta \dot{p}(t') \, dt' - \mu \omega_0^2 \delta \ddot{q}(t) \]  

where \( \mu \omega_0^2 = V''(q) \) corresponding to the harmonic mode. The above equations (4.1) and (4.3) can then be solved by Laplace transformation technique to obtain

\[ \delta \dot{p}(t) = \frac{1}{\mu} \delta \dot{p}(0) \, C_v(t) + \delta \ddot{q}(0) \, C_q(t) \]  

where

\[ C_v(t) = L^{-1} \left[ \frac{1}{s^2 + s \bar{\gamma}(s) + \omega_0^2} \right] \]  

and

\[ C_q(t) = 1 - \omega_0^2 \int_0^t C_v(t') \, dt' \]
and $\tilde{\gamma}(s)$ is the Laplace transform of $\gamma(t)$ defined as $\tilde{\gamma}(s) = \int_0^\infty \gamma(t)e^{-st}dt$. After squaring and quantum mechanical averaging Eq.(4.4) yields

$$\langle \delta \dot{q}^2(t) \rangle = \frac{1}{\mu^2} \langle \delta \dot{p}^2(0) \rangle \langle \delta \dot{q}^2(t) \rangle + \frac{1}{\mu} \langle \delta \dot{p}(t) \rangle \langle \delta \dot{q}(0) \rangle + \langle \delta \dot{q}(0) \delta \dot{q}(0) + \delta \dot{q}(0) \delta \dot{p}(0) \rangle$$

(4.7)

For a minimum uncertainty state we chose

$$\langle \delta \dot{p}^2(0) \rangle = \frac{\mu \hbar \omega_0}{2}, \quad \langle \delta \dot{q}^2(0) \rangle = \frac{\hbar}{2\mu \omega_0} \quad \text{and} \quad \langle \delta \dot{p}(0) \delta \dot{q}(0) + \delta \dot{q}(0) \delta \dot{p}(0) \rangle = 0$$

(4.8)

Furthermore we assume the form of the spectral density function, $J(\omega)$, as,

$$J(\omega) = \frac{1}{4} \frac{\gamma}{\omega}$$

(4.9)

where $\gamma$ is the static dissipation constant.

Using Eqs.(2.4), (2.22) and (4.9) in the continuum limit we have

$$\gamma(t) = \frac{1}{2} \gamma \delta(t)$$

(4.10)

Laplace transform results in

$$\gamma(s) = \gamma_1$$

(4.11)

where $\gamma_1 = \gamma/2$.

Now with the form of $\gamma(s)$ as given by Eq.(4.11) the relaxation functions $C_v(t)$ and $C_q(t)$ become

$$C_v(t) = \frac{1}{2\omega_1} \left[ e^{-s_1 t} - e^{-s_2 t} \right]$$

(4.12)

$$C_q(t) = \frac{\omega_1^2}{2\omega_1} \left[ \frac{1}{s_1} e^{-s_1 t} - \frac{1}{s_2} e^{-s_2 t} \right]$$

(4.13)

where,

$$\omega_1 = \left( \frac{\gamma_1^2}{4} - \omega_0^2 \right)^{1/2}, \quad s_1 = \frac{\gamma_1}{2} - \omega_1, \quad s_2 = \frac{\gamma_1}{2} + \omega_1$$

(4.14)
Making use of Eq. (4.8), (4.12) and (4.13) in (4.8) we obtain quantum correction term $B_2(t)(= \langle \delta \hat{q}^2(t) \rangle)$ as

$$B_2(t) = \frac{\hbar \omega_0}{8 \mu \omega^2} \left[ \left( 1 + \frac{\omega_0^2}{s_1^2} \right) e^{-2s_1 t} + \left( 1 + \frac{\omega_0^2}{s_2^2} \right) e^{-2s_2 t} - 4e^{-\gamma_1 t} \right]$$ (4.15)

The above term can be utilized in the integral of the second term in Eq. (3.12) for its explicit evaluation to find out the dependence of the system parameters on the dephasing rate analytically. For better accuracy the systematic corrections to higher order can be worked out as discussed in detail in Refs. [18-24].

V. VIBRATIONAL DEPHASING RATE; COMPARISON WITH EXPERIMENTS AND DISCUSSION

Having obtained the explicit expression for the leading order contribution $B_2(t)$ from Eq. (4.15) we are now in a position to write down the total quantum vibrational dephasing rate. To this end we make use of Eq. (4.15) in the second term and Eq. (4.9) in first term of the expression (3.12) and obtain, after some algebra,

$$\kappa_{dep} = \kappa_1 + \kappa_2$$ (5.1)

with

$$\kappa_1 = \frac{9 k_{111}^2 \gamma}{4 \pi \omega_0^2} \int_0^\infty dt \int_0^\infty d\omega \frac{\hbar \omega}{(\omega^2 - \omega_0^2)^2} \coth \left( \frac{\hbar \omega}{2k_B T} \right) \cos(\omega t)$$ (5.2)

and

$$\kappa_2 = \frac{81 \hbar^2 k_{111}^4 \gamma}{16 \omega_0^{10}}$$ (5.3)

The vibrational dephasing time can be defined as

$$\tau_v = \frac{1}{\kappa_{dep}}$$ (5.4)

The expression (5.1) is the central result of this paper. We already pointed out that $\kappa_2$ is a new contribution of quantum origin due to nonlinearity of the system potential. $\kappa_1$ in the limit $k_B T \gg \hbar \omega_0$ is the standard well known expression for the classical dephasing rate. It is important to note that $\kappa_1$ incorporates quantum effect due to heat bath only. Although
both $\kappa_1$ and $\kappa_2$ are dependent on nonlinearity, $\kappa_2$ vanishes in the classical limit and is also independent of temperature. The temperature dependence of the dephasing rate is due to the first term $\kappa_1$ of Eq.(5.2). It is important to note that at very low temperature as the integrand $\frac{1}{2}\hbar \omega \coth(\frac{\hbar \omega}{2k_BT})$ in $\kappa_1$ reduces to $\frac{1}{2}\hbar \omega$, the temperature independent vacuum limit, one observes that the dephasing caused by anharmonicity of the vibrational mode does not vanish even at absolute zero because of the contributions of these two terms. This aspect of temperature independence of the width of the transition from the ground state had been noted earlier in Ref.[5]. The origin of the temperature independence in $\kappa_2$ and the nature of dephasing may be traced to the second term in Eq.(3.8) which results from the third term of the normal mode Hamiltonian Eq.(3.2). This term contains the quantum contribution to nonlinear potential explicitly calculated in terms of $B_2(t)$ in Sec.IV. This lowest order quantum fluctuation (or uncertainty) is independent of the quantum character of the heat bath and also temperature and causes frequency fluctuation leading to dephasing and therefore a homogeneous broadening of the transition similar to natural linewidth. In order to assess the relative contribution of the two terms in the total dephasing rate we estimate the numerical magnitude of these two quantities as well as the dephasing time for three diatomic molecules, $N_2$, $O_2$ and $CO$ and compare them with experimental results obtained from either picosecond pump-probe technique or from Raman linewidth measurement of liquids using interferometric techniques. We have also studied the rate as a function of temperature away from critical point or triple point of these liquids and compared with experiments.

The values of the parameters essential for calculation of the dephasing rate using formulae are given in the Table 1. Apart from mass $\mu$, frequency of the fundamental $\omega_0$, size $r$, at a temperature $T$ two sensitive parameters are the static friction due to the liquid, $\gamma$, and the anharmonic force constant $k_{111}$. Although use of local viscosity which formally takes into account of wave vector dependence of the viscosity for the size of the probe has been advocated for calculation of friction, we confine ourselves to standard Stoke’s expression ($\gamma = 6\pi \eta r / \mu$, $\eta$ being viscosity coefficient of the liquid). For diatomics we determine $k_{111}$ from the spectroscopic constants $\alpha_e$ and $B_e$ using $k_{111} = -\frac{\hbar \omega_0^2}{4\mu^{1/2}B_e r^2} (1 + \frac{\alpha_e \omega_0}{6B_e^2})$. The integrals in are calculated numerically for all the three cases. The magnitudes of $\kappa_1$ and $\kappa_2$ are shown separately in the table along with the percentage contribution of $\kappa_2$ in the total dephasing rate $\kappa_{dep}$. Three pertinent points are to be noted. First, it is well known that classical
dephasing rate (i.e. $\kappa_1$ in the classical limit) is higher than the corresponding quantum rate $\kappa_1$. This is somewhat reminiscent of the quantum suppression of classical values of rate co-efficient for the thermally activated processes for shallow cubic potentials\cite{31}. Second, it is evident that just as in the classical theory, anharmonicity contributes significantly to the total quantum dephasing rate. In case of $N_2$ it is as large as $\sim 26.5$ percent of total dephasing rate. The dephasing time thus calculated corresponds fairly to that obtained from experiments. Third, the quantum effects due to heat bath appears quite significantly through the integrals in $\kappa_1$. This is because, the frequency dependence of the integrand is quite sharp at around $\omega_0$ as a result of the the frequency denominator ($\omega^2 - \omega_0^2$) and $\hbar \omega_0 \gg k_B T$ for these molecules. Therefore the diatomic oscillator behaves more closely as a quantum oscillator rather than its classical counterpart.

The temperature dependence of the dephasing rate according to Eq.\cite{5,11} has been compared for the set of parameter values mentioned in the Table 1 to that obtained from experiments\cite{16,17} in Fig.1 for the molecules $N_2$, $O_2$ and $CO$. While the experimental results span a wide range of temperatures covering triple point and critical point, we confine ourselves in the region away from the points of phase transition, since the present theory is outside the scope of phase transition. We find a linear dependence of dephasing rate on temperature which is a fair agreement with experimental observations\cite{16,17}.

VI. CONCLUSION

Based on a quantum Langevin equation and the corresponding Hamiltonian formulation within a c-number description, we have calculated quantum vibrational dephasing rate for a cubic oscillator system using first order perturbation technique and compared the results with experiments. It is shown that the vibrational dephasing rate comprises of two terms. The first term is the standard expression obtained earlier by several workers using independent approaches and is reduces to its classical limit as $k_B T \gg \hbar \omega_0$. This term is responsible for finite temperature dependence of the dephasing rate. The second term, an essential content and offshoot of the present theory, is a leading quantum correction due to nonlinearity of the system potential which contributes quite effectively to the total dephasing rate. Keeping in view of this observation, we believe that this quantum correction term is likely to play a significant role in triatomic and polyatomic molecules as well.
Acknowledgement

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Figure Captions

Fig.1: Variation of vibrational dephasing rate (FWHM) with temperature (T) for the set of parameter values mentioned in the Table 1 and comparison with experiments for three different diatomics $N_2$ (▲ experiment$^{16}$; dotted line, theory), $O_2$ (● experiment$^{16}$; dashed line, theory) and $CO$ (■ experiment$^{17}$; bold line, theory).
Table 1. Quantum vibrational dephasing rate: comparison between theory and experiment for diaatomic molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\omega_0$ (cm$^{-1}$)</th>
<th>$T$ (°K)</th>
<th>$r$ (10$^{-8}$ cm)</th>
<th>$\mu$ (10$^{-23}$ g)</th>
<th>$\eta$ (cP)</th>
<th>$k_{111}$ (10$^{48}$ g$^{-1/2}$cm$^{-1}$s$^{-2}$)</th>
<th>$k_1$ (10$^9$ s$^{-1}$)</th>
<th>$k_2$ (10$^9$ s$^{-1}$)</th>
<th>$k_{dep}$ (10$^9$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>2326</td>
<td>77</td>
<td>1.107</td>
<td>1.16304</td>
<td>0.158</td>
<td>7.47955</td>
<td>5.2965</td>
<td>1.90446</td>
<td>7.200</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1552</td>
<td>90</td>
<td>1.345</td>
<td>1.32824</td>
<td>0.190</td>
<td>3.01</td>
<td>14.5996</td>
<td>3.6535</td>
<td>18.253</td>
</tr>
<tr>
<td>CO</td>
<td>2170</td>
<td>77</td>
<td>1.214</td>
<td>1.13904</td>
<td>0.17157</td>
<td>8.1601</td>
<td>11.6269</td>
<td>6.5691</td>
<td>18.19</td>
</tr>
</tbody>
</table>

$^a$Present theory
$^b$Oxtoby’s classical theory [Ref.(3) and (4)]
$^c$Experiment [reference (12) and (14)]
$^d$Experiment [reference (15)]