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Short-Time Behavior of the Vibrational-Energy–Time Correlation Function for a One-Dimensional Model of Diatomic Molecules

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The short-time behavior of the vibrational-energy–time correlation function (VECF) is studied both theoretically and numerically for a one-dimensional model of diatomic molecules with harmonic intramolecular and hard intermolecular interactions. In the equipartition regime, the short-time expansion of the VECF is independent of the vibrational frequency and agrees with statistical mechanics.

KEY WORDS: One-dimensional dynamical system; vibrational-energy correlation function; energy transfer; short-time expansion; diatomic molecule.

1. INTRODUCTION

In this paper we study the vibrational-energy–time correlation function (VECF) for a one-dimensional model of diatomic molecules with harmonic intramolecular and hard intermolecular interactions, introduced in ref. 1 and further investigated in ref. 2. The study of this quantity was first considered by Benettin *et al.*$^{(3)}$ for a model similar to ours, but with a soft repulsive intermolecular interaction. They used the VECF to determine the effectiveness of the energy exchange between translational and vibrational degrees of freedom. Since the decay of the VECF was nonexponential, with a slow long-time decrease, they considered the half-time of the decay and observed an exponential increase of it with the frequency of the internal vibration. Later on the VECF was computed for the model of diatomic molecules with hard interactions by Erpenbeck and Cohen,$^{(1)}$ where an

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apparently exponential decay at early times was found, with no indication of a slow, post-exponential decay increasing with the frequency.

The main purpose of this paper is to study the initial decay of the VECF for our system of diatomic molecules by using a statistical mechanical calculation of the VECF short-time behavior and to show that the leading term in t is indeed independent of the frequency. This statistical mechanical prediction will then be compared with the results of the numerical calculations. The VECF is studied numerically for different values of the number of molecules n and of the frequency ω. For sufficiently large values of n and ω, when the system exhibits equipartition of energy,(1,2) we find agreement between the observed initial decay of the VECF and the statistical mechanical result. As the border between the equipartition and no-equipartition regions in the (n, ω) parameter space is approached, deviations occur from this statistical mechanical behavior.

2. VECF FOR A ONE-DIMENSIONAL MODEL OF DIATOMIC MOLECULES

We consider a one-dimensional model of n identical diatomic molecules. Each molecule consists of two atoms of mass m bound together by an intramolecular harmonic force. Of the two atoms in a molecule only one interacts with an atom in a nearest neighbor molecule, while the other atom is transparent for all other atoms, including that in the same molecule, with which it interacts harmonically. Denoting the position and the momentum of the interacting atom in molecule i by q_i and p_i, respectively, and the position and momentum of the transparent atom by q'_i and p'_i, respectively, we consider for each molecule center-of-mass and relative coordinates and momenta:

$$\begin{aligned} Q_i &= \tfrac{1}{2}(q_i + q'_i) \qquad & P_i &= \tfrac{1}{2}(p_i + p'_i) \\ \xi_i &= \tfrac{1}{2}(q_i - q'_i) \qquad & \pi_i &= \tfrac{1}{2}(p_i - p'_i) \end{aligned} \tag{1}$$

and write the Hamiltonian for the system as

$$H = \sum_{i=1}^{n} \frac{P_i^2}{m} + \sum_{i=1}^{n} \frac{\pi_i^2}{m} + m\Omega^2 \sum_{i=1}^{n} \xi_i^2 + U_I \tag{2}$$

where Ω is the intramolecular harmonic frequency, and U_I is the intermolecular interaction potential, which we choose to be that of hard points, i.e., of the form

$$U_I = \sum_{i<j}^{n} U_{\text{hp}}(Q_i + \xi_i - Q_j - \xi_j); \quad U_{\text{hp}}(r) = \begin{cases} \infty & \text{if } r = 0 \\ 0 & \text{if } r > 0 \end{cases} \tag{3}$$

The n diatomic molecules can move on the infinite line, with a basic cell of length L and periodic boundary conditions. Details on the definition of the system and on the determination of its evolution can be found in ref. 1.

On the right-hand side of (2), the first term represents the translational (kinetic) energy E_t of the center of mass of the molecules, and the second and the third terms the kinetic E_{vk} and potential E_{vp} contributions to the vibrational energy E_v, respectively. Associated with the Hamiltonian H are, apart from the total energy E, characteristic units of length $l_0 = L/n$, mass $m_0 = m$, and time $t_0 = (L/n)(E/nm)^{-1/2}$, so that a reduced frequency can be defined by $\omega = \Omega t_0$.

The vibrational-energy–time correlation function is defined by

$$c_v(t) = \langle E_v(0)\, E_v(t) \rangle \tag{4}$$

where $\langle \cdots \rangle$ denotes an ensemble average. It is convenient to consider the normalized VECF:

$$\rho_v(t) = \frac{c_v(t) - \langle E_v \rangle^2}{c_v(0) - \langle E_v \rangle^2} \tag{5}$$

which is expected to decay from an initial value of unity toward zero at long times when statistical mechanics applies.

For the system of diatomic molecules with soft intermolecular interactions considered by Benettin *et al.*, the decay in time of the vibrational-energy correlation function appeared to be slower than exponential, as confirmed by subsequent calculations on the same model by Erpenbeck and Cohen.(4) The decay time of the VECF was defined as its half-life, which was found to increase exponentially with the frequency. This result is in agreement with Jeans' conjecture of an exponential dependence of energy-sharing time scales on the frequency of the diatomic molecules.(5)

Even though the dependence on ω of the decay of the VECF in the soft interaction case is not completely clear yet,(4) it is obvious that a crucial difference arises when a hard potential is considered. For the soft interaction, the duration of a collision defines a time scale. With increasing frequency the intramolecular vibrational motion and the translational motion become increasingly weakly coupled, making the exchange of energy between internal and external degrees of freedom increasingly difficult and ineffective. For the hard interaction, on the other hand, the collisions are instantaneous and such a time scale vanishes. No matter how large ω, then, vibrational and translational motions are strongly coupled, and an effective exchange of energy between them always occurs. The role played by the hard collisions will become clear in the following section, where the calculation of the initial slope of the VECF will be reduced to a binary collision calculation and no dependence on the frequency will appear.

3. SHORT-TIME BEHAVIOR OF THE VECF

For the statistical mechanical calculation of $\rho_v(t)$, Eq. (5), it is convenient to consider our system of diatomic molecules in equilibrium in the "volume" L, at temperature T, as a system of n hard points of mass m coupled by a harmonic force to n "ghost" points of mass m. Therefore, we rewrite the Hamiltonian (2) as a function of $\{p_i, p'_i, q_i, q'_i\}$, $i=1,\ldots, n$:

$$H=\sum_{i=1}^{n}\left\{\frac{p_i^2}{2m}+\frac{p_i'^2}{2m}\right\}+\frac{m\Omega^2}{4}\sum_{i=1}^{n}(q_i-q'_i)^2+U_I \tag{6}$$

where now U_I is a function of $q^n=\{q_1,\ldots, q_n\}$ only.

We describe the system of n hard points and n ghost points in equilibrium by a canonical ensemble at temperature $T=2\langle E\rangle/3nk_{\mathrm{B}}$, where $\langle E\rangle=E$ is the total energy and k_{B} the Boltzmann constant.

In the following we consider the short-time expansion of $\rho_v(t)$:

$$\rho_v(t)=\rho_v(0)+\rho'_v(0)\,t+\mathcal{O}(t^2) \tag{7}$$

where $\rho_v(0)=1$. We derive an expression for the initial slope $\rho'_v(0)$ as a canonical ensemble average involving the Liouville operator, which we then calculate.

First, we consider the Liouville operator $\mathscr{L}$, which generates the time evolution of a dynamical function f via:

$$f(\Gamma;t)=e^{t\mathscr{L}}f(\Gamma;0) \tag{8}$$

For the system of n hard points and n ghost points the Liouville operator is given by

$$\mathscr{L}=\mathscr{L}_0+\mathscr{T} \tag{9}$$

where

$$\mathscr{L}_0=\sum_{i=1}^{n}\left\{\frac{p_i}{m}\frac{\partial}{\partial q_i}+\frac{p'_i}{m}\frac{\partial}{\partial q'_i}+\frac{m\Omega^2}{2}(q_i-q'_i)\left(\frac{\partial}{\partial p_i}-\frac{\partial}{\partial p'_i}\right)\right\} \tag{10}$$

is the free Liouville operator (whose three terms describe the free streaming of the hard points, the free streaming of the ghost points, and the time evolution due to the internal harmonic interaction, respectively), and

$$\mathscr{T}=\frac{1}{2}\sum_{i,j}^{n}\mathscr{T}(i,j) \tag{11}$$

where $\mathscr{T}(i, j)$ is the binary collision operator describing the collision $i \leftrightarrow j$. We observe that the free Liouville operator $\mathscr{L}_0$ is anti-Hermitian, and that $\mathscr{T}(i, j)$ has the following properties:

$$\mathscr{T}(i, i) = 0, \qquad \mathscr{T}(i, j) = \mathscr{T}(j, i) \tag{12}$$

In one dimension the binary collision operator is given by$^{(6)}$

$$\mathscr{T}(i, j) = \frac{1}{m}\,\delta(q_{ij})\,|p_{ij}|\,\Theta(p_{ij})[b(i, j) - 1] \tag{13}$$

where $p_{ij} = p_i - p_j$, $q_{ij} = q_i - q_j$, Θ is the unit step function, and the operator $b(i, j)$, defined by

$$b(i, j)\,p_i = p_j, \qquad b(i, j)\,p_j = p_i \tag{14}$$

describes the exchange of momenta in a binary collision. Moreover, in one dimension $\mathscr{T}(i, j) \neq 0$ only if $j = i + 1$, and therefore the $\mathscr{T}$ operator becomes

$$\mathscr{T} = \sum_{i=1}^{n} \mathscr{T}(i, i + 1) \tag{15}$$

Second, for the short-time expansion of $\rho_v(t)$ it is useful to introduce the fluctuation $\mathscr{E}_v$ of E_v:

$$\mathscr{E}_v = E_v - \langle E_v \rangle \tag{16}$$

Then, by indicating with $\mathscr{E}_v^{(i)}$ the contribution of the ith molecule to $\mathscr{E}_v$, we have

$$\mathscr{E}_v = \sum_{i=1}^{n} \mathscr{E}_v^{(i)} \tag{17}$$

with $\langle \mathscr{E}_v^{(i)} \rangle = 0$ and $\langle \mathscr{E}_v^2 \rangle = n\langle (\mathscr{E}_v^{(i)})^2 \rangle$. The normalized VECF (5) can then be rewritten as

$$\rho_v(t) = \frac{\langle \mathscr{E}_v e^{t\mathscr{L}} \mathscr{E}_v \rangle}{\langle \mathscr{E}_v^2 \rangle} \tag{18}$$

Expanding around $t = 0$, we obtain for the initial slope

$$\rho_v'(0) = \frac{\langle \mathscr{E}_v \mathscr{L} \mathscr{E}_v \rangle}{\langle \mathscr{E}_v^2 \rangle} \tag{19}$$

Using now that $\mathcal{L}_0$ is anti-Hermitian, we have,

$$\langle \mathcal{E}_v \mathcal{L} \mathcal{E}_v \rangle = \langle \mathcal{E}_v \mathcal{T} \mathcal{E}_v \rangle \tag{20}$$

and using Eq. (11) and the properties of $\mathcal{T}(i, j)$, Eq. (12), we obtain

$$\langle \mathcal{E}_v \mathcal{T} \mathcal{E}_v \rangle = 2n\{\langle \mathcal{E}_v^{(1)} \mathcal{T}(1,2)\, \mathcal{E}_v^{(1)} \rangle + \langle \mathcal{E}_v^{(2)} \mathcal{T}(1,2)\, \mathcal{E}_v^{(1)} \rangle\} \tag{21}$$

Then, from Eqs. (19)–(21), the initial slope $\rho_v'(0)$ becomes

$$\rho_v'(0) = \frac{2}{\langle (\mathcal{E}_v^{(1)})^2 \rangle} \{A_s + A_d\} \tag{22}$$

where

$$\begin{aligned} A_s &= \langle \mathcal{E}_v^{(1)} \mathcal{T}(1,2)\, \mathcal{E}_v^{(1)} \rangle \\ A_d &= \langle \mathcal{E}_v^{(2)} \mathcal{T}(1,2)\, \mathcal{E}_v^{(1)} \rangle \end{aligned} \tag{23}$$

In this way the calculation of $\rho_v'(0)$ is reduced to a two-molecule calculation. After a little algebra we obtain

$$\begin{aligned} A_s &= -\frac{1}{8m^3} \langle \delta(q_{12})\, \Theta(p_r)\, |p_r|^3\, (P_T^2 + p_1'^2) \rangle \\ A_d &= \frac{1}{8m^3} \langle \delta(q_{12})\, \Theta(p_r)\, |p_r|^3\, P_T^2 \rangle \end{aligned} \tag{24}$$

where $p_r = p_{12} = p_1 - p_2$, and $P_T = \frac{1}{2}(p_1 + p_2)$. We observe that $\langle \delta(q_{12}) \rangle = \langle \delta(q_{12}) \rangle_{\mathrm{hp}}$, where $\langle \cdots \rangle_{\mathrm{hp}}$ is the canonical ensemble average relative to a system of n hard points only. In fact, the average of any microscopic function, which depends only on the phases of the hard points, for the model including the ghost points is equal to that for the pure hard-point model.(6) Moreover, we have

$$\langle \delta(q_{12}) \rangle = \langle \delta(q_{12}) \rangle_{\mathrm{hp}} = \frac{n}{L}\, g_{\mathrm{hp}}(0) \tag{25}$$

where $g_{\mathrm{hp}}(r)$ is the pair correlation function for the system of pure points.(6) Evaluating the other canonical averages in (24) and using that, in the thermodynamic limit, $g_{\mathrm{hp}}(0) = 1$,(7) we find

$$\begin{aligned} A_s &= -\frac{3(n/L)}{4\beta^2 (\pi \beta m)^{1/2}} \\ A_s &= \frac{(n/L)}{4\beta^2 (\pi \beta m)^{1/2}} \end{aligned} \tag{26}$$

Finally, from (22), using (26) and $\langle \mathscr{E}_v^{(1)^2} \rangle = 1/\beta^2$, we obtain

$$\rho_v'(0) = -\left(\frac{2}{3\pi}\right)^{1/2} t_0^{-1} \tag{27}$$

Thus, the short-time expansion for ρ_v as a function of the reduced time $\tau = t/t_0$ is given by

$$\rho_v(\tau) = 1 - \left(\frac{2}{3\pi}\right)^{1/2} \tau + \mathcal{O}(\tau^2) \tag{28}$$

4. NUMERICAL CALCULATIONS AND RESULTS

In the definition (5) of $\rho_v(t)$ phase averages are considered. In numerical statistical mechanics[8] one invokes the quasi-ergodic hypothesis, which implies the equivalence of time averages with the corresponding ensemble averages. The natural choice of the equilibrium ensemble for our system is the molecular dynamics (MD) ensemble, characterized by given values of the parameters n, L, E as well as the total momentum P. By using the quasi-ergodic hypothesis, we estimate $\rho_v(t)$ by the time average $\bar{\rho}_v(t)$ along a single (long) trajectory. It should be remarked that the statistical mechanical calculation of the previous section, leading to Eq. (28), was carried out using the canonical ensemble and equivalence with the MD ensemble is obtained, strictly speaking, in the thermodynamic limit only.

The numerical calculation of $\bar{\rho}_v(t)$ was carried out in the usual way.[8] The vibrational energy $E_v(t)$ is "observed" at discrete times and on each trajectory the correlation function is obtained as a time average over a set of "time origins." Statistical uncertainties are determined by using coarse-grained time averaging. Standard tests for statistical control[9] are performed, i.e., the coarse-grained observations are tested to be randomly chosen samples from a normal distribution, and when these tests are satisfied we compute the standard deviation of the mean from the sample variance. We remark that our analysis is based on the assumption of ergodic behavior of the trajectory, and the statistical tests are expected to fail in the case of periodic or quasiperiodic motion.

A typical example of quasiperiodic, i.e., nonergodic, motion is shown in Fig. 1, where $\rho_v(t)$ is plotted for a system with $n = 3$ and $\omega = 0.01$. In this case there is no equipartition of energy and the statistical analysis failed. Phase averages and time averages cannot be interchanged, and $\rho_v(t)$, which is a time average along a single trajectory, depends on the initial phase. We observe that $\rho_v(t)$ takes on positive as well as negative values.

On the other hand, the results of the previous section on the initial slope of $\rho_v(t)$ are expected to be valid only when statistical mechanics applies. We have studied the decay of the VECF for a large number of different realizations with n and ω chosen in the equipartition region.[3] We always observed an initial exponential decay of ρ_v with a characteristic time of $\sim 2t_0$, essentially independent of ω. In Fig. 2 we compare the initial exponential decay of ρ_v with the theoretical value (27) for systems of 100 molecules at different frequencies. The agreement between theory and numerical calculations is seen to be good. The weak oscillatory behavior of the observed values of $\ln \rho_v(t)$ around the theoretical curve is apparently related to the time origin spacing used in the calculation and to a resulting strong serial correlation for $\rho_v(t)$ at nearby values of the time.(8) In view of the large statistical uncertainties, though, this oscillation is not statistically significant.[4]

For times greater than a few mean free times t_0 we observed deviations from the exponential decay, similar to those of the velocity autocorrelation function for a gas of hard spheres.(10) We can therefore write $\rho_v(t)$ in the following way:

$$\rho_v(t) = \rho_{v,0}(t) + \rho_{v,1}(t) \tag{29}$$

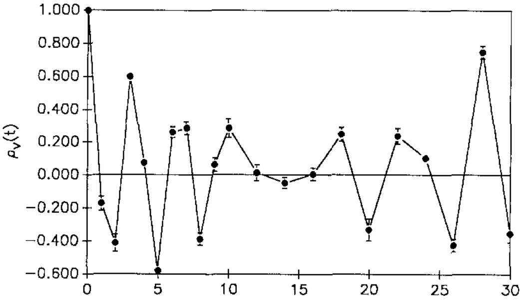

Fig. 1. Plot of $\rho_v(t)$ for $n = 3$ and $\omega = 0.01$.

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[3] The equipartition region is roughly $n > 20$, $\omega > 1$. More precisely, from earlier calculations(2) we have that for fixed n and small enough ω there is no equipartition. As ω becomes larger, the system shows equipartition and the value of ω for this to occur decreases when n is increased.

[4] The statistical uncertainties for $\bar{\rho}_v(t)$ were obtained by coarse-graining the data into $S = 30$ samples. We estimated the statistical precision for $\ln \bar{\rho}_v(t)$ by using $\ln(\bar{\rho}_v \pm \varepsilon) \approx \ln \bar{\rho}_v \pm \varepsilon/\bar{\rho}_v$. We also considered $\overline{\ln \rho_v}$ by further coarse-graining into $S' = 3$ samples, obtaining essentially the same behavior as observed for $\ln \bar{\rho}_v$, i.e., the mean and the statistical uncertainties are similar.

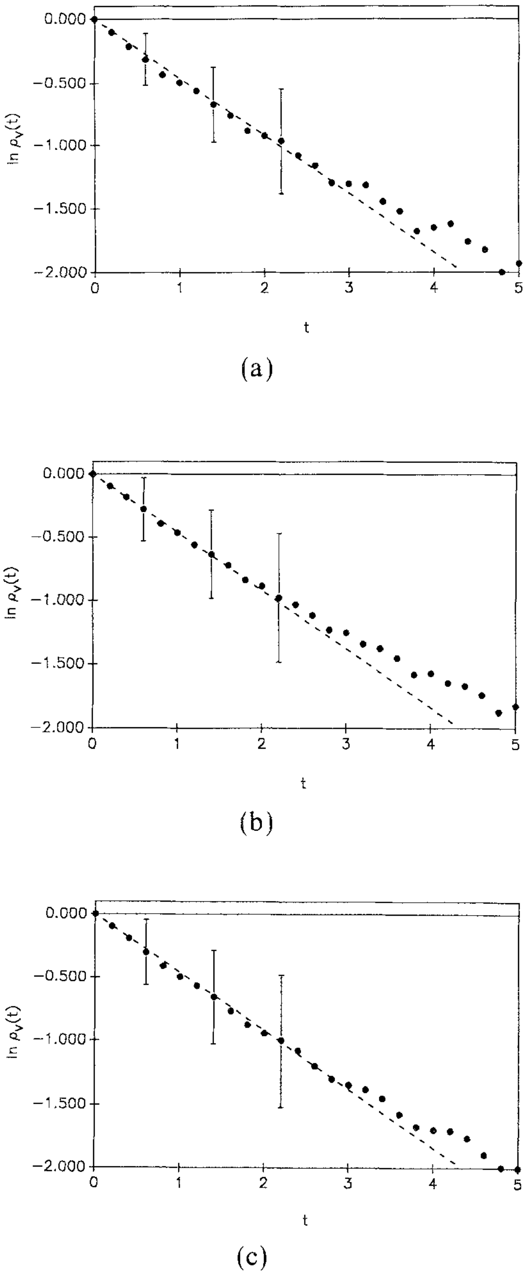

Fig. 2. Plot of $\ln \rho_v(t)$ for $n = 100$ and (a) $\omega = 100$, (b) $\omega = 1000$, and (c) $\omega = 2000$. The dashed line represents the theoretical prediction (28).

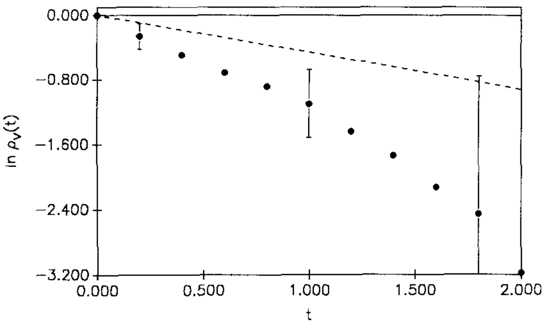

Fig. 3. Plot of ln $\rho_v(t)$ for $n=100$ and $\omega=1$. The dashed line represents the theoretical prediction (28).

where $\rho_{v,0}(t)$ represents the initial exponential decay independent of ω, and $\rho_{v,1}(t)$ gives nonexponential contributions for larger times, which are expected to depend on ω. Even though this dependence was not investigated, it should be remarked that $\rho_{v,1}(t)$ is essentially 0 for $t \leqslant 2t_0$, and at most of the order of 10^{-3}.

The values of n and ω considered in Fig. 2 are well inside the equipartition region. If we approach the border of the equipartition region by keeping $n=100$ fixed and by decreasing ω, we observe deviations from the statistical mechanical result. As an example, in Fig. 3 we plot ln $\rho_v(t)$ versus time for $n=100$ and $\omega=1$ and we can see that ρ_v shows an initial decay rate larger than the one for $n=100$ and ω in the range 100–2000 (cf. Fig. 2). These deviations from statistical mechanical behavior increase with decreasing ω.

5. CONCLUSIONS

We have used statistical mechanics to compute the short-time behavior of the vibrational-energy–time correlation function for our model of diatomic molecules with hard interactions, and we have compared these predictions with the numerical results.

When equipartition holds, we find that the initial decay of the VECF is exponential and independent of ω. We remark that our theoretical study of the short-time behavior of the VECF was based on the use of the canonical ensemble and the results apply to the MD ensemble as well in the thermodynamic limit. Nevertheless, our numerical calculations show that a good agreement is already achieved for $n=100$. Our results show that, for n and ω large enough, there is no anomaly in the exchange of vibrational and translational energy, which should be contrasted to what is found for the model of Benettin *et al.*(3)

When the border between the equipartition and the no-equipartition regions is approached, deviations from the predicted statistical mechanical behavior are observed. We remark that the initial exponential decay of the VECF predicted by statistical mechanics is consistent with the behavior with respect to equipartition only "deep" in the (n, ω) equipartition region. The observed deviations for the VECF appear already in the region where approximate equipartition is obtained (as shown, for example, in Fig. 3). It would be interesting to study these deviations systematically (in particular with respect to large n) and to see how the behavior of the VECF could be used as a test for statistical mechanical behavior, additional to equipartition.

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