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On the delocalization of the C nuclei in the C₆₀ molecule; a Feynman path-integral Monte Carlo study

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Abstract. Feynman path-integral Monte Carlo simulations have been performed to study finite-temperature properties of the C₆₀ molecule in a temperature range between 50 and 800 K. The interaction between the C atoms was modelled by the empirical Tersoff potential that reliably reproduces several properties of fullerenes like the binding energy and the alternation between the long and short C–C bonds. We show that the delocalization of the C nuclei is comparable to the difference between the lengths of the long and short bonds. The importance of quantum effects for the C nuclei is illustrated by comparing classical and quantum results for properties like the total energy and the radial and angular distribution functions.

The non-conventional molecular and solid-state properties of fullerenes have been the focus of comprehensive research activities of experimental and theoretical groups [1, 2]. The superconductivity observed in alkali-doped C₆₀ materials inspired detailed work on the strength of the electron–phonon coupling, because BCS pairing has been assumed in many contributions [3]. In this context the vibrational properties of these compounds have been analysed as well [4]. Previous theoretical studies on the structure and dynamics of C₆₀ can be divided into two groups. The first one consists of electronic structure investigations that describe the electronic interaction in different degrees of sophistication but without including thermal effects (i.e. $T = 0$ K calculations) [3, 5]. In the second group, T -dependent properties are obtained by simulations based on Monte Carlo (MC) and molecular dynamics (MD) methods [6]. However, in these simulations the interatomic interactions are usually parametrized by empirical functions that depend on the coordinates of the nuclei. Midway between these two groups are Car–Parrinello methods [7] that combine a quantum description for the electrons with a classical one for the nuclei [8].

The light mass of the carbon atoms may lead to the *a priori* suggestion that quantum effects (e.g. zero-point vibrations) are of particular importance for fullerenes. Zero-point-motion effects in C₆₀ and C₇₀ have been studied within the harmonic approximation [9, 10]. The harmonic frequencies were obtained from classical trajectories generated by the Car–Parrinello method. Many-body effects related to anharmonicity in the internuclear potential are completely neglected in such an approach. Therefore we have investigated finite-temperature properties of an isolated C₆₀ molecule that depend on the atomic nuclei with a quantum many-body approach. Our analysis is based on the Feynman path-integral (PI) technique that has become a powerful method for deriving statistical mechanical properties of quantum systems [11, 12]. PI simulations are important in including the non-trivial

influence of quantum nature on thermodynamic and static properties of condensed matter. In the present work we discuss the total energy E , the delocalization properties of the nuclei (D_i) and their radial and angular distribution functions (rdf, adf) as a function of temperature. In previous work we have used PI simulations to study pure and doped crystalline silicon [13, 14], and the phase diagram of the one-dimensional (1D) Hubbard chain [15].

The general background of Feynman PI simulations can be found in the literature [11, 12]. Therefore we only summarize those principles that are necessary to follow our discussion. One key step of the present approach is the mapping of the partition function of the quantum system (here: atomic nuclei of the C_{60} molecule) onto a classical one, that thus can be studied by the classical MC or MD simulation techniques. In the present work the carbon atoms of C_{60} are treated as quantum particles that interact through an effective many-body potential. We have employed the empirical potential of Tersoff that has been designed to describe the energetics and structure of numerous polytypes of carbon [16]. The partition function Z of the quantum system with P particles at temperature T is given by the trace of the statistical density matrix $\rho(\mathbf{R}, \mathbf{R}'; \beta)$:

$$Z = \text{Tr} [e^{-\beta H}] = \text{Tr} [\rho(\mathbf{R}, \mathbf{R}'; \beta)] \quad (1)$$

with H standing for Hamiltonian and $\beta = (k_B T)^{-1}$ (k_B = Boltzmann constant). \mathbf{R} and \mathbf{R}' are vectors in a $3P$ -dimensional space, whose components are the cartesian coordinates of the nuclei. The path-integral evaluation of Z can be performed through the discretization of the density matrix along a cyclic path composed of N steps as symbolized in (2):

$$Z = \int \prod_{j=1}^N d\mathbf{R}_j \rho \left(\mathbf{R}_1, \mathbf{R}_2; \frac{\beta}{N} \right) \rho \left(\mathbf{R}_2, \mathbf{R}_3; \frac{\beta}{N} \right) \cdots \rho \left(\mathbf{R}_N, \mathbf{R}_1; \frac{\beta}{N} \right). \quad (2)$$

For sufficiently large N the density matrix $\rho(\mathbf{R}_j, \mathbf{R}_{j+1}; \beta/N)$ can be evaluated within the high-temperature approximation by a free-particle propagator, leading to the following expression for the partition function of the quantum system:

$$Z \approx \left(\frac{Nm}{2\pi\beta\hbar^2} \right)^{3PN/2} \int \prod_{j=1}^N d\mathbf{R}_j \exp \left\{ -\beta \sum_{j=1}^N \left[\frac{1}{2} k (\mathbf{R}_{j+1} - \mathbf{R}_j)^2 + N^{-1} V(\mathbf{R}_j) \right] \right\} \quad (3)$$

where

$$(\mathbf{R}_{j+1} - \mathbf{R}_j)^2 = \sum_{p=1}^P (r_{p(j+1)} - r_{pj})^2 \quad (4)$$

$$k = \frac{Nm}{\beta^2 \hbar^2}. \quad (5)$$

The vector r_{pj} in (4) stands for the position of carbon atom p and j labels the coordinate along the path. m is the carbon mass and V the potential energy part of the Hamiltonian. Path-integral decomposition of the density matrix requires the cyclic boundary condition $\mathbf{R}_{N+1} = \mathbf{R}_1$. Relation (3) can be considered as an expression for the partition function of a classical system with cyclic chains of particles interacting through a harmonic potential. The paths of a carbon nucleus are described by a cyclic chain that is divided into N 'time-slices'. Within a given chain the carbon nucleus at the time-slice j is 'harmonically coupled' to its $j+1$ and $j-1$ images. The associated spring constant k has been defined in equation (5). Interchain interactions via the potential V require the same j argument in both chains. The interaction is equal to the one corresponding to the quantum particles, $V(\mathbf{R}_j)$, but divided by a factor N (number of time-slices). In equation (3), distinguishable particles have been assumed. We believe that this set-up is a physically reasonable description for

atomic nuclei, since the overlap of the nuclear wave functions is negligible due to the large mass of the nuclei.

To derive the finite-temperature properties of the C₆₀ molecule we have employed the classical Metropolis MC sampling algorithm [17]. The canonical partition function Z has been sampled according to equation (3) with $V(\mathbf{R}_i)$ given by the empirical Tersoff potential [16]. At each temperature studied we generated 6×10^4 quantum paths per atom for the calculation of ensemble-averaged properties, and 10^4 quantum paths for system equilibration. The number N of time-slices at temperature T was fixed by the condition $NT = 3000$ K, an approximation that ensures convergence in the total energy with an error less than 3% at 50 K. The Tersoff potential conserves the icosahedral I_h symmetry of the C₆₀ molecule. The experimental bond-length alternation of 5 pm between (6-5) and (6-6) bonds is reproduced almost quantitatively. For the minimum-energy configuration of the C₆₀ molecule we find a length of 150 pm for the 60 long (6-5) bonds, of 146 pm for the 30 short (6-6) bonds, and a molecular diameter of 737 pm. These bond lengths exceed the experimental values of 144.6 pm and 140.2 pm by about 5 pm. The experimental diameter is 706 pm [18]. The potential energy per atom in the minimum-energy configuration was -6.73 eV. Subsequently we have taken this value as zero for the potential energy.

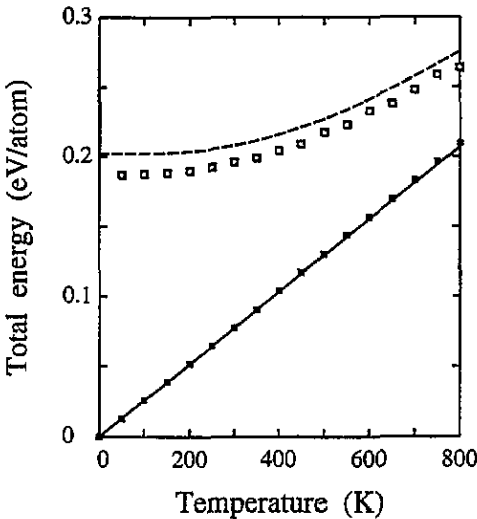


Figure 1. The temperature dependence of the total energy E of a C₆₀ molecule. Open and filled squares are values obtained by quantum and classical simulations. The broken curve is derived from the experimental phonon density of states $\rho_{\text{exp}}(\omega)$ in the harmonic approximation, while the full line is the classical harmonic result ($E = 3k_B T$).

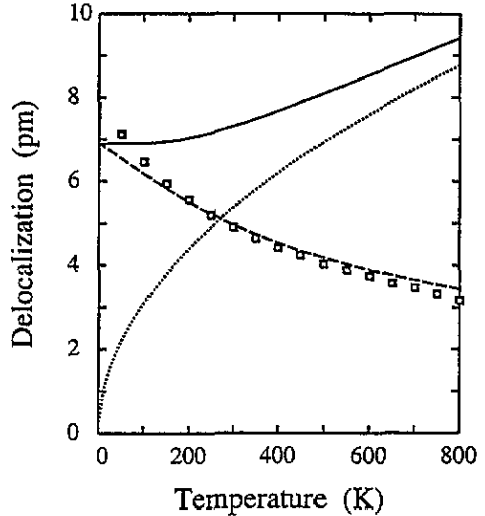


Figure 2. Delocalization of the C nuclei as a function of temperature. The full (D_q) and dotted (D_c) curves are derived from the experimental phonon spectrum within a quantum and a classical harmonic approximation. The squares are simulation results for the quantum delocalization D_q^{PI} . The broken line is the value of D_q as derived from the phonon spectrum.

In figure 1 we show the temperature dependence of the total energy E of the C₆₀ molecule obtained in the PI simulation (empty squares) together with the classical value (filled squares) that has been obtained by setting $N = 1$ in the calculations. The total energy of a classical harmonic oscillator (ho) ($E = 3k_B T$) is shown by a full line in the figure. The total energy E is roughly constant between 0 and 300 K suggesting that only zero-point

vibrations are relevant in this temperature range. The zero-point energy amounts to 0.184 eV per atom. The deviation between the classical result and the quantum simulation is large and shows the importance of quantum effects. We compare our PI results with properties like the total energy and the delocalization of the C nuclei that can be derived from the experimental phonon density of states $\rho_{\text{exp}}(\omega)$ of C_{60} measured by neutron scattering [19]. Within the harmonic approximation the total energy E is given by:

$$E = 3 \int_0^{\infty} d\omega \hbar\omega \left[\bar{n}(\omega) + \frac{1}{2} \right] \rho_{\text{exp}}(\omega). \quad (6)$$

The average number of excited phonons of frequency ω , $\bar{n}(\omega)$, has been derived by using the Bose-Einstein formula:

$$\bar{n}(\omega) = \left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1 \right]^{-1}. \quad (7)$$

The broken line in figure 1 has been evaluated on the basis of equation (6). We find a T -independent deviation between this curve and our PI results. The zero-point energy derived from $\rho_{\text{exp}}(\omega)$ amounts to 0.202 eV, a value that differs by 9% from that obtained in the simulation. This discrepancy may be due to the difference between the phonon density of states corresponding to the Tersoff potential and the experimental $\rho_{\text{exp}}(\omega)$ and also to anharmonic effects that are appreciable even at low temperatures. These anharmonic effects are evident from the fragmentation of the total energy into potential and kinetic energy contributions. At 50 K we find in the quantum PI simulation that the kinetic energy is 5 % smaller than the potential one. However, in a harmonic approximation both kinetic and potential energies should be equal.

It is of some interest to compare the differences in the delocalization expected for C nuclei in the C_{60} molecule in a quantum and a classical treatment. The delocalization D_t including quantum and thermal degrees of freedom can be defined as the root mean square deviation of the nucleus coordinate r_p around its equilibrium position (\bar{r}_p) :

$$D_t = \sqrt{\overline{r_p^2} - (\bar{r}_p)^2}. \quad (8)$$

The angular brackets represent ensemble-averaged values at a given temperature. \bar{r}_p stands for the centre of gravity of the path coordinate sampled for nucleus p in C_{60} :

$$\bar{r}_p = N^{-1} \sum_{j=1}^N r_{pj} \quad (9)$$

and $\overline{r_p^2}$ is defined as:

$$\overline{r_p^2} = N^{-1} \sum_{j=1}^N r_{pj}^2. \quad (10)$$

For a quantum harmonic oscillator the temperature dependence of the delocalization D_t can be worked out explicitly [12]:

$$D_t^{\text{ho}} = \sqrt{\frac{3\hbar}{2m\omega} \coth\left(\frac{\hbar\omega}{2k_B T}\right)}. \quad (11)$$

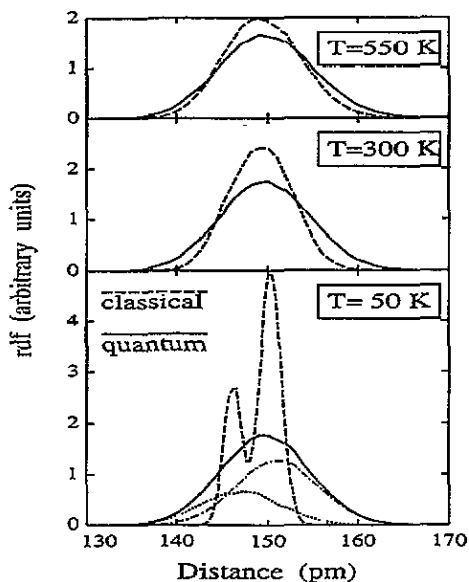


Figure 3. The radial distribution function (rdf) for the C nuclei at distances corresponding to nearest C neighbours at three different temperatures. Full curves are the results of quantum simulations; broken curves represent the classical limit. The quantum curve at 50 K has been resolved into two distributions corresponding to the long (6-5) and short (6-6) bonds (dash-dotted and dotted curves).

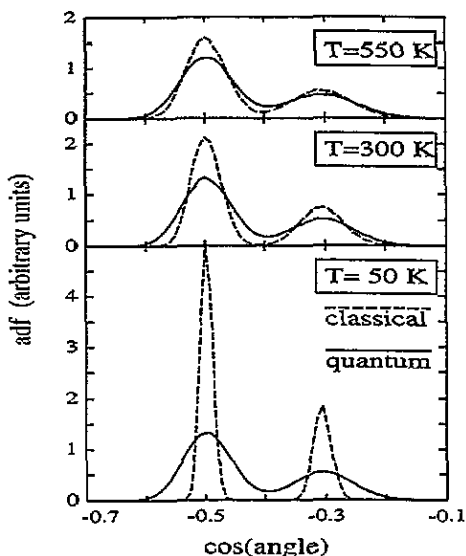


Figure 4. The angular distribution function (adf) encountered in the C₆₀ molecule at three different temperatures. Full curves are the results of quantum simulations; broken curves represent the classical limit.

We employ the label D_c for the delocalization corresponding to a classical treatment. For the harmonic oscillator a classical approach leads to a delocalization D_c^{ho} with the following temperature dependence:

$$D_c^{ho} = \sqrt{\frac{3k_B T}{m\omega^2}} \tag{12}$$

In figure 2 we display the values of D_t and D_c for the C nuclei obtained by weighting the results of (11) and (12) with the phonon density of states $\rho_{exp}(\omega)$. The full line corresponds to D_t and the dotted one to D_c . As a convenient measure of quantum effects related to the nuclei we define the ‘quantum’ delocalization D_q as:

$$D_q = \sqrt{D_t^2 - D_c^2} \tag{13}$$

For a harmonic oscillator the quantum delocalization D_q can be set equal to D_q^{PI} , equation (14). This parameter has a simple physical interpretation within the PI formalism. It corresponds to the root mean square radius of the cyclic paths that describe the quantum particle:

$$D_q^{PI} = \sqrt{\langle \overline{r_p^2} \rangle - \langle \overline{r_p} \rangle^2} \tag{14}$$

The values of D_q^{PI} obtained in the PI simulation are shown by open squares in figure 2, while the broken curve symbolizes the corresponding quantity derived from the experimental

$\rho_{\text{exp}}(\omega)$. Two important remarks can be extracted from the results shown in figure 2. First, the delocalization D_t of the C nuclei is large, about 7 pm at low temperatures, a value that is of the same order as the difference (5 pm) between the length of the (6–5) and the (6–6) bonds. The second point is that a classical treatment does not describe adequately the delocalization properties of the C nuclei even at temperatures as high as room temperature. The D_t -value reported in [9] is about 7 pm at $T = 0$ K, in close agreement to our own results. We recall that the data of Kohanoff *et al* [9] were derived within the harmonic approximation for internuclear potentials corresponding to density functional calculations. In the present work we have simplified the internuclear potential by using the empirical Tersoff potential, but an ‘exact’ quantum many-body description has been employed for the dynamics of the C nuclei in the fullerene molecule.

In figures 3 and 4 the radial and angular distribution functions rdf and adf are displayed for three temperatures. Again we have compared the results of quantum and classical simulations. Only the low-temperature classical rdf shows two distinct maxima corresponding to the long and short C–C bonds; note the ratio of 2:1 between (6–5) and (6–6) bonds. Quantum delocalization leads to a single peak formed by two strongly overlapping curves. In contrast to the T -dependent classical rdf, the rdf obtained in the quantum simulation is almost T independent. We wish to point out that the latter rdf curves coincide with the experimental curve derived from neutron scattering experiments in the sense that only one unresolved peak is present for distances corresponding to nearest C neighbours [20]. Also the adfs given in figure 4 show large broadening of the distribution because of quantum fluctuations. The two peak maxima correspond to the bond angles of the six- and five-membered rings of C_{60} . With increasing temperature the difference between classical and quantum distribution functions is reduced. Nevertheless figures 3 and 4 prove that quantum phenomena related to the C nuclei are still sizeable at room temperature. The high delocalization of the C atoms suggests that theoretical approaches assuming fixed nuclei seem to be a rough approximation only. The importance of quantum effects on the dynamics of the C nuclei has been already assessed by Kohanoff *et al* [9] on the basis of a harmonic approximation. We have shown by PI simulation that those results are still valid when anharmonic effects are taken into account. We believe that the strong quantum delocalization derived for C_{60} may also be important for the superconducting pairing [21].

Acknowledgments

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