Fractal dimension as a scaling law for nuclear quantum effects: a neutron Compton scattering study on carbon allotropes

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Abstract. In this work, we tackle the problem of the sensitivity of neutron Compton scattering, measured through the widths of nuclear momentum distributions, to the degree of complexity and ordering of the structural motif characterising the surrounding environment felt by a particular nucleus (carbon). In doing so, we replace the usual concept of the bond strength categorised in terms of its thermodynamical or electronic properties with a novel observable inspired by the language of mathematical topology, the Hausdorff-Besicovitch fractal dimension. We derive a relatively straightforward connection between the fractal dimension of a given system under consideration and the nuclear kinetic energy. To achieve this, we modify the concept of the energy equipartition theorem for solid-state systems composed of carbon atoms where the atom-ordering topology does not follow a simple two or three-dimensional order, but rather atoms are placed along curves in space that have an intermediate dimension related to the varying amounts of information they contain. A series of results from past neutron Compton scattering studies, as well as new results on Buckminsterfullerene (C\(_{60}\)), correlate with the topological measures of surface roughness and bending, as categorised quantitatively by the fractal dimension of the system. Namely, for the same formal chemical binding motif (sp\(^2\)C) and with decreasing system dimensionality from nearly 3 towards 1, the quantum nature of the system becomes more pronounced. The simple scaling law developed in this work allows for relatively simple assessment of the nuclear “quantumness” of a given system with potentially important ramifications in the \textit{ab initio} modelling of nuclear quantum effects in condensed matter.

One must say- instead of points, straight lines and planes - tables, chairs and beer mugs

David Hilbert.
1. Introduction

From the point of view of a materials chemist, Neutron Compton scattering (NCS) can be termed as “nuclear quantum thermometry” of condensed matter systems and molecules [1–3]. As a neutron spectroscopic technique, NCS owes its unique character to its capability to measure, in a mass-resolved manner, nuclear momentum distributions (NMDs). NMDs are, in turn, the most basic quantum observables that can be related to nuclear quantum effects (NQEs) [1–3].

In fact, NMDs of light and medium-weight atomic species are dominated by the zero-point-energy contribution to the nuclear kinetic energies [1–3]. Mathematically, the second moments of NMDs are proportional to the first-moments of atom-projected vibrational densities of states (apVDOS). Consequently, the NMD widths, from the \textit{ab initio} modelling methodology point-of-view, can be computed by optimising the geometry of a given system of atoms or molecules, e.g. in a crystal, and computing the apVDOS. This relatively simple mathematical procedure has profound physical ramifications. Namely, by virtue of the closure relation for the quantum harmonic oscillator (QHE), this route of calculation of the NMDs can be termed as being due to “trivial nuclear quantum effects”. This name is fully deserved as NMDs turn out to be in this case completely computable by resorting to electronic structure theory dictating the properties of the forces entering the dynamical matrix, used further to compute the apVDOS [4]. Furthermore, by comparing the NMD width predicted using apVDOS, obtained from \textit{ab initio} calculation performed at a given temperature, with its counterpart form an NCS experiment one can assess the degree in which “trivial nuclear quantum effects” determine NMD of a given nucleus. This computational route has got very important ramifications for heavy-weight nuclei, whose NMD widths are almost entirely dictated by their respective apVDOS. Thus, the “non-trivial nuclear quantum effects”, such as nuclear wave function coherence and nuclear quantum tunnelling, contribute to NMDs of heavy-weight nuclei in such a minuscule manner that their contribution can be neglected with impunity. Conversely, for light-to-medium weight both “trivial” and “non-trivial nuclear quantum effects” may simultaneously shape the NMDs and the interplay between them is, in general, dictated by the system temperature and nuclear mass.

Are then the NQEs exhibited by heavy-weight nuclei completely obscured from the view of the NCS? The answer to this question can only be given after a systematic search of available heavy-weight NMD data for condensed-matter systems has been performed and correlations between NQE-related properties and NCS observables are established. Such a systematic review of NCS has recently been published [1,3]. Despite the fact that some degree of correlation has been observed between the formal electric charge of the nuclei in lattice sites, their electronegativity, the character of bonding (covalent, ionic, metallic, or long-range dispersive) and the widths of NMDs, the full picture is still largely missing.

One of the main questions still remaining to be addressed is how the degree of complexity and ordering of the structural motif characterising the surrounding environment felt by a particular nucleus correlates with its NMD shape. For instance, it is not clear what level of sensitivity the technique has to length scales characterising phenomena such as dynamical or static disorder, surface roughness or the dimensionality of a condensed-matter system. The sensitivity of NCS to first-order structural phase changes is generally believed to be very high [1,3], as the local environment of the atom is changed during the transition. In the case of dynamical disorder, however, there may be no change in the average local environment, or it may involve a continuous change with temperature. It is also not clear what is the critical length-scale attributed to a dynamic or static distortion in a condensed-matter system or imperfection of the crystal lattice that can lead to a visible change of the nuclear kinetic energy with reference to a perfectly ordered system. It is also not clear how this critical length-scale depends on the dimensionality of the system, its temperature, the nuclear mass and the chemical binding motif dominating the surrounding of a given nucleus. These open questions have largely motivated the work presented here.
As the correlations mentioned above may be obscured by a number of different, often cross-correlated factors, the optimal experimental protocol should seek to establish links between the topological features of a family of systems exhibiting the same chemical binding motif. The chemistry of carbon offers a great opportunity in this respect as one can easily identify a large family of carbonaceous systems, all of which will be characterised by the sp² hybridisation. Amongst carbonaceous systems, Buckminsterfullerene (C₆₀) represents a particularly interesting case. It is characterised by dynamical disorder in a wide range of temperatures and it undergoes two phase transitions. At high temperature (>260 K), C₆₀ forms a face-centered-cubic structure, where the C₆₀ molecules are able to perform isotropic free rotation about their lattice sites. Below 260 K, the system undergoes a first-order phase transition to a simple cubic structure with orientational anisotropy. Below 90 K, all rotational motion ceases to exist, and the system becomes trapped in a given orientation.

In addition to C₆₀ serving as a prototypical system for studying dynamical disorder, it also represents a system of geometric curiosity from a nuclear kinetic energy perspective. C₆₀ is quasi-2D quantum system in the sense that the C₆₀ molecules themselves can be best thought of as folded 2D sheets. This means that the shape of carbon NMDs in solid C₆₀ should be simultaneously dictated by the vibrational properties of planar carbon systems and by the librations and translations associated with the entire C₆₀ molecules. In this sense, C₆₀ falls into the hierarchy somewhere between a 2D-system like graphene and a 3D-system like graphite.

In what follows, we compare a series of relatively simple carbon-based compounds, bulk carbon, two-dimensional carbon sheets, and C₆₀ with the aim to place them on a common scale characterising the degree of the correlation between the complexity of the structural motif characterising the surrounding environment felt the carbon and its kinetic energy. To this end, we will attempt to use a geometrical scale, well-suited for nanoscale systems, the fractal dimension.

2. Methodology
2.1. Ab initio methods
As the ab initio methods, whose results were used in this work to calculate carbon apVDOS and carbon NMDs in both low and high-temperature phases of solid C₆₀, are very well known and described in great detail elsewhere, here only a brief account of the methodology employed will be given.

In the solid state from the sublimation temperature, 800 K, down to 260 K, C₆₀ undergoes rapid rotation (10 ps at room temperature) and the structure can be approximated as a face centred cubic (fcc) lattice of spheres, space group Fm3m with one molecule in the primitive cell [5]. Below 260 K, an ordered simple cubic (sc) phase is obtained, space group Pa3 with four molecules in the primitive cell [6]. For the low-temperature ordered phase the ab initio work, reported in the literature, essentially exactly reproduces the structure from neutron diffraction work [6]. However, as noted by Parker et al. [6], in order to simulate the high-temperature disordered C₆₀ phase, a computationally intractable periodic-DFT calculation using a very large unit cell consisting of many disordered C₆₀ molecules would be required. It is, however, possible to use an ordered fcc phase with space group Fm3m that can be obtained by aligning the three twofold axes along the Cartesian x, y and z-axes [7]. In order to prevent an unphysical expansion of the lattice, due to van der Waals-nature of this solid C₆₀ phase, the the ab initio geometry optimisation needs to be carried out at the experimental lattice parameter of 14.160 Å [6].

Thus, as an input for our spectroscopic calculations reported in this work we have used the output generated from the existing results of the ab initio work by Parker et al. who performed periodic DFT calculations of both crystalline structures using the plane-wave pseudopotential method implemented in the CASTEP code [6]. Exchange and correlation were approximated using the PBE functional, and a norm-conserving pseudopotential for carbon
was generated using the kinetic-energy optimised method with a plane-wave cut-off energy of 750 eV. The equilibrium structure was obtained by Broyden-Fletcher-Goldfarb-Shanno (BFGS) geometry optimization algorithm with the residual-force-convergence within 0.0015 eV Å$^{-1}$. In light of practically dispersion-less phonon spectra, observed both at the spectroscopic and computational level, phonon frequencies for this study were obtained by diagonalisation of dynamical matrices computed using density-functional perturbation theory at zero wave-vector (Γ-point-LD calculation) [6].

Interestingly, in the context of the topological analysis presented in this work, yet another method of apVDOS calculation is worth mentioning, namely the recursion method [8]. The recursion method is based on a theorem stating that the projected density of states is stable with respect to changes in distant parts of the system and that it can be calculated recursively by tri-diagonalising the dynamical matrix describing the forces in a basis of orthonormal operators [8]. Mathematically, the diagonal elements of the dynamical matrix, $D$, are solved for using recursive equations [8]. In case of the solid C$_{60}$, $D$ depends on the geometry of the C$_{60}$ molecule, the mass of the carbon nucleus, and four force constants used to model the four bonds formed between a given carbon and its nearest neighbours. The recursion method has been demonstrated to satisfactorily reproduce the apVDOS of carbon in molecular C$_{60}$ using two of the four force constants to model the stretching of the pentagonal and hexagonal bonds, respectively, and the remaining two force constants to model the bending of the pentagonal and hexagonal bonds, respectively.

2.2. From ab initio calculations to NMD observables

Predictions of the widths of the NMDs for nuclei in molecular crystals can be calculated using two computational routes:

- the lattice dynamics (LD) computational route, whereby one performs ab initio calculation [usually within the density functional theory (DFT) under the Born-Oppenheimer approximation] consisting of geometry optimisation, followed by solving the eigenproblem of the dynamical matrix of the whole crystal and calculation of phonon-dispersion curves for both intra and intermolecular modes [3,9];
- a mode-decoupling route, whereby one neglects the rotation-vibration interactions and any interplay between translational and internal motion which enables the decomposition of the nuclear kinetic energy into three separate contributions: molecular translations and librations (referred to as external contributions), and internal molecular vibrations [10,11] which can be accounted for using two different types ab initio calculations: (i) a single-molecule geometry optimisation followed by vibrational analysis, or (ii) a dispersion-less Γ-point LD calculation.

As presented in more detail in Ref. [9], the first route amounts to the calculation of the second moment of an NMD for a nucleus of mass, $M$, $\sigma_M(r)^2$, that can then be decomposed into three Cartesian directions in space, for which a unit vector $r = (x, y, z)$ can be defined, according to:

\[
\sigma_M(r)^2 = \frac{M^2}{N_q \hbar^2} \sum_{q \in BZ} \sum_{\lambda=1}^{N_\lambda} |e(\lambda, q) \cdot r|^2 \frac{\hbar \omega_\lambda}{2} \coth \left( \frac{\hbar \omega_\lambda}{2k_BT} \right),
\]

where $\omega(\lambda, q)$ are phonon frequencies, $e(\lambda, q)$ are polarization vectors and $T$ is the sample temperature, and $k_B$ the Boltzmann constant. The double summation in Eq. (1) runs over all $N_q$ vectors in the first Brillouin zone, and all phonon branches $N_{\lambda}$.

In the second route the computation of $\sigma_M(r)^2$ is performed under the assumptions that (1) molecular librations can be dealt with classically, (2) vibrational displacements of nuclei from their equilibrium positions are small if compared with their average distances from the centre
of mass, and (3) internal vibrations can be considered as purely harmonic and treated quantum mechanically [10,11]. The translational contribution to the kinetic energy of a nucleus of a mass $M$ reads:

$$\langle E^{\text{tra}}_k \rangle = \frac{1}{2} \frac{M}{M_T} \dot{v}_{CM}^2,$$

(2)

where $v_{CM}$ is the molecule center-of-mass velocity and $M_T$ is the total mass of the molecule. Making use of the classical equipartition theorem, we obtain

$$\langle E^{\text{tra}}_k \rangle = \frac{3}{2} \frac{M}{M_T} k_B T.$$

In case of librations in the solid, the contribution to the kinetic energy $\langle E^{\text{lib}}_k \rangle$ of a nucleus of a mass $M$ in a molecule can be expressed, in the coordinate system coinciding with the molecular principal inertia axes, in the following way:

$$\langle E^{\text{lib}}_k \rangle = \frac{1}{2} M \dot{p}_r = \frac{3}{2} \frac{M}{M_T} k_B T \sum_{i,j=1}^{3} r_i R_{ij} r_j,$$

(3)

where the tensor $R_{ij}$ is closely linked with the Sachs–Teller (S-T) mass tensor [10,11] for $M$, which often appears in the classical treatment of molecular rotations:

$$M_{ij}^{-1} = R_{ij} + M_T^{-1} \delta_{ij}.$$

(4)

The contribution to $\sigma_M^2(r)$ from Eqs. 2 and 3 can then be defined as:

$$\sigma_{S-T}^2(r) = \frac{M^2 k_B T}{\hbar^2} \left( \frac{1}{M_T} + \sum_{i,j=1}^{3} r_i R_{ij} r_j \right).$$

(5)

The internal vibrational contribution to the kinetic energy, $\langle E^{\text{vib}}_k \rangle$ can be worked out decomposing the nuclear displacements, $u_M$ into normal modes $q_\lambda$ by means of the amplitude vectors $C_\lambda^M$:

$$u_M = \sum_{\lambda=1}^{N_\lambda} C_\lambda^M q_\lambda.$$

(6)

The variance $\sigma_M(r)^2$ for $r$ parallel to the direction of the nuclear momentum $p$ can be calculated using the following relation [10,11]:

$$\sigma_{\text{intra}}^2(r) = \frac{M^2}{\hbar^2} \sum_{\lambda=1}^{N} (C_\lambda^M)^2 \sum_{j=1}^{N_\lambda} \frac{1}{N_\lambda} \frac{\hbar \omega_j^\lambda}{4} \coth \left( \frac{\hbar \omega_j^\lambda}{2 k_B T} \right),$$

(7)

where $\hbar \omega_j^\lambda$ is the harmonic excitation energy of the $j$-th component of the $\lambda$-th mode, and $N_\lambda$ is the number of components of the same mode [10,11].

The multivariate Gaussian vibrational contribution, $\sigma_M^2(r)$ can be chosen so as to coincide with the molecular principal inertia axes, and combining Eqs. 5 and 7 one has [10,11]:

$$\sigma_M^2(r) = \sigma_{S-T}^2(r) + \sigma_{\text{intra}}^2(r),$$

(8)

from which the spherically averaged value of the second moment of the nuclear momentum distribution for a given nucleus $\sigma_M(r)^2$ can be calculated [12]:

$$\sigma_M^2 = \frac{1}{3} \left[ \sigma_M(x)^2 + \sigma_M(y)^2 + \sigma_M(z)^2 \right].$$

(9)
2.3. Nuclear momentum distributions from NCS

Detailed accounts of the NCS method, both in terms of its instrumental and mathematical foundations, can be found elsewhere [1–3]. Here, we will only emphasize the aspects of the method that, in our opinion, guide the reader to a better understanding of the results of the concurrent measurements using inelastic (INS) and NCS spectroscopy presented in this work. In an nutshell, the kinematics of NCS leads to the description of the scattering in terms of the Impulse Approximation (IA), whereby a billiard-ball type of collision of neutrons with individual nuclei in the sample leads to instantaneous excitation of all nuclear degrees of freedom. Moreover, the energy and momentum conservation, invoked by the IA, leads to a description in which each binary collision of a neutron with an individual nucleus produces a separate recoil peak in the time-of-flight spectrum [1–3].

It is this mass selectivity that underlies the very uniqueness of NCS as a spectroscopic method. For a given fixed sample stoichiometry, the intensity of the NCS recoil peak of each nuclear isotope present in the sample scales only as the product of the total bound scattering cross-section and the relative quantity of this particular isotope [1–3]. A very important consequence of this scaling is that the shape of the NMD of each nuclear isotope is not affected by the scattering cross sections and the relative quantities of other isotopes from the same sample. Thus, there is no mixing of neutronic responses of different isotopes as NCS, unlike INS, is free from the complication of “neutron-weighting”. This “neutron weighting” implies that, unlike in NCS, in INS in order to reproduce an experimental spectrum one must calculate a linear combination of apVDOS curves, predicted for each individual isotope by an ab initio calculation, weighted by the neutron scattering cross-sections of each isotope. This important distinction between INS and NCS has many consequences. The one that is most explored in the NCS literature is that the second moment of the NMD for a given isotope is only proportional to the first moment of its apVDOS [1–3].

In the time-of-flight (TOF) domain, $t$, and for a given fixed scattering angle, $\theta$, the NCS spectrum, $C_{\theta}(t)$, is described as:

$$ C_{\theta}(t) = A^t \left[ \frac{E_0 I(E_0)}{Q} \right]_{t} \times \sum_{n=1}^{N} I_n M_n J_n[y_n(t)] \otimes R_n[y_n(t)]. $$

Mathematically, the mass selectivity of the NCS method can be expressed by the fact that the whole expression, $C_{\theta}(t)$, can be further decomposed into subexpressions describing spectral contributions of recoil peaks of individual isotopes, $J_n[y_n(t)] \otimes R_n[y_n(t)]$. This decomposition is facilitated by another unique feature of NCS, West scaling [1–3]. In a nutshell, West scaling is a consequence of the conservation of momentum and energy during a binary collision of a neutron with a nucleus of mass $M$, and it reduces the shape of the curve describing the recoil peak of $M$ to a peak function, mathematically expressed as $(M_N/h^2Q(t)) J_N(y_{MN(t)}) \otimes R_n[y_n(t)]$, which is centered at the recoil energy $E_r = h^2Q^2/2M$ with $h = 2.0446$ (meV amu)$^{1/2}$ A [2,13–19]. It is this very function $J(y(t))$ in this expression which is a peak function expressed in a domain of the West scaling variable $y(t) = (M_N/h^2Q(t)) \left( (E_0(t) - E_1 - h^2Q(t)^2/2M \right)$, where $E_1$ is the final neutron energy which is fixed in an inverted-geometry instrument (thus $t$-independent). Physically, $J_N(y_{MN})$ is the so called NCS profile [13,14] and formally corresponds to the longitudinal NMD of the target nucleus along $y_{MN}$. Instrumentally, each recoil peak is represented by the convolution of the NMD of a given nucleus with the nucleus-specific instrument resolution function, which can also be expressed in the domain of the West scaling variable of a given mass $M$ [1–3].

The fact that the width of the Vesuvio resolution function increases rapidly with increasing mass of the recoiling nucleus [20] renders fitting anisotropic NMD models to experimental NCS data, recorded for nuclei with masses higher than few atomic mass units, practically infeasible.
In consequence, carbon NMDs are usually fitted by spatially averaged, Gaussian distributions, despite the fact that the \textit{ab initio} modelling predicts usually anisotropic carbon NMDs. In this case, \( J_{IA}(y) \) for a given mass \( M \) in the IA limit depends only on the magnitude of \( y \) but not on \( \dot{Q} \), described in the IA limit, by a purely Gaussian term only:

\[
J_{IA}(y) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{y^2}{2\sigma^2} \right),
\]

where \( \sigma \), the standard deviation (STD) of the NMD, with the present choice of units, is expressed in units of Å\(^{-1}\).

For finite values of \( Q \), corrections to the IA are known as “Final-State Effects” (FSEs) \([2,19]\) and must be applied. Usually, the longitudinal NMD in the presence of the FSEs corrections is expressed as a series of the form:

\[
J(y) = J_{IA}(y) + J_{FSE}(y) = J_{IA}(y) - \frac{M \langle \nabla^2 V \rangle}{36\hbar^2 \kappaq^2} J_{IA}(y) + ..., \tag{12}
\]

where \( J_{IA}(y) \) is the IA result given by Eq. (11). \( \langle \nabla^2 V \rangle \) is the mean value of the Laplacian of the potential energy of the nucleus expressed in meV Å\(^{-2}\) (cf. Refs. \([19,21]\)).

An explicit connection between the FSE magnitude \( k \) and \( \sigma \) can be established in the harmonic approximation, \( k = \sigma \sqrt{\frac{\tau}{2}} \) \([22–24]\) with the FSE term, given by the Eq. 12, expressed using the third order Hermite polynomial, \( H_3 \left( \frac{y}{\sigma \sqrt{2}} \right) \):

\[
J(y) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{y^2}{2\sigma^2} \right) \left[ 1 - \frac{\sigma \sqrt{\tau}}{2} \frac{\sqrt{2}}{Q} H_3 \left( \frac{y}{\sigma \sqrt{2}} \right) \right]. \tag{13}
\]

3. INS and NCS results for solid C\(_{60}\)

3.1. Carbon vibrational density of states and INS

As a starting point for our later discussion we show the results of the application of the recursion method for the calculation of the carbon apVDOS in an isolated C\(_{60}\) molecule taken from the existing in the literature work \([8]\). The apVDOS calculated in this manner (see Figure 1) was reported to have a reasonable qualitative agreement with the experiments considering that the Raman and infrared spectra are related to the VDOS through matrix elements whose exact nature is imprecisely known \([8]\).

Following the brief account of the results of the recursion method, we give a short account of the high resolution inelastic neutron scattering (INS) at the inverted geometry neutron spectrometer TOSCA at ISIS spanning energy transfers up to 4000 cm\(^{-1}\) \([25–27]\). The spectral resolution of TOSCA is similar to that of infrared and Raman techniques, approximately 2\% of the energy in question. The measurements were performed on 5 g of C\(_{60}\) as bought from Sigma Aldrich using a flat aluminum cell of cross-sectional area 4x4.8 cm\(^2\). The sample was studied at a temperature of 10 K using a dedicated closed-cycle helium refrigerator, so as to minimize the effect of the Debye-Waller factor, thus allowing us to fully distinguish the individual peaks. Data were reduced using the Mantid Software \([28]\). The INS spectrum of low-temperature phase of C\(_{60}\) recorded at TOSCA is shown in Figure 2. The experimental spectrum is compared in Figure 2 with the synthetic spectrum generated from the output of the \textit{ab initio} periodic-DFT LD calculation performed for the low-temperature phase of C\(_{60}\) by Parker \textit{et al.} \([6]\), briefly described in section 2.1.
Figure 1. The result of the application of the recursion method to the solution of the dynamical matrix equation for the C$_{60}$ molecule, taken from Ref. [8]. See text for further details.

Figure 2. The INS spectrum of C$_{60}$, recorded at the inverted geometry neutron spectrometer TOSCA, at the ISIS Pulsed Neutron and Muon Source, Rutherford Appleton Laboratory, United Kingdom (black trace) compared with the synthetic spectrum generated from the output of the the *ab initio* periodic-DFT LD calculation by Parker *et al.* [6] (read trace). See text for further details.
3.2. Nuclear kinetic energy of carbon in solid C\textsubscript{60} from NCS

All NCS measurements were performed on the latest incarnation of the indirect-geometry NCS spectrometer VESUVIO located at the ISIS Pulsed Neutron and Muon Source, United Kingdom [20,29,30]. The NCS forward scattering data reduction performed in this work follows the literature protocol [9]. In short, the protocol amounted to the sequential, detector-by-detector, pre-fit of the data, the calculation of sample-dependent signal corrections (multiple scattering and gamma background), the focusing of corrected data in the West scaling space of carbon, and finally the fit of the focused data to obtain the longitudinal carbon NMDs, from which the values of the second moments and kinetic energies of carbon were calculated.

For the VESUVIO experiment on C\textsubscript{60}, the sample was a pellet of C\textsubscript{60} in powder form. The specimens were enclosed in a 6x6 cm\textsuperscript{2} flat aluminum (Al) cell resulting in a 92% transmission level of the sample in the Al container, and 2% transmission level of the empty Al container, respectively. The data used in the analysis were recorded in the temperature range 5–300 K, with the sample temperature stabilised using a dedicated helium closed-cycle refrigerator.

In the final NCS data analysis step, a maximum-likelihood-based model selection was performed, based on the Bayesian approach implemented in the Fabada algorithm in the MantidPlot software [31]. Examples of the results of the application of this procedure for C\textsubscript{60} are shown in Figure 3. Inspired by our previous NCS work [32] two NMD models were compared: (i) a model in which the NMD is described by a purely Gaussian shape, and (ii) an NMD model described mathematically by a sum of a Gaussian function and a Gaussian multiplied by a fourth-order Hermite polynomial accounting for the extra peakedness (excess kurtosis) of the NMD (not shown here). The Bayesian analysis preferred the purely Gaussian NMD model for NCS data recorded at every temperature between 5 K and 270 K. The probability-distribution-function (PDF) histograms of standard deviations of purely Gaussian NMDs, \(\sigma\), calculated using the Fabada algorithm for carbon NCS data recorded at 5 different temperatures, are shown in Fig. 3. The inset of Fig. 3 shows carbon NMD recorded at 5 K (blue trace) together with the fitted Gaussian NMD curve (red dashed trace). The values of the standard deviations of purely Gaussian NMDs, \(\sigma\), calculated using the Fabada algorithm, are listed in Table 1 and denoted as “Experiment”. These values are compared in Table 1 with lattice dynamics (LD) DFT predictions, calculated using Eq. (1) from the output of the DFT-based phonon calculation [6] and denoted as “DFT”, and the values obtained from the recursive method, denoted as “Recursive”.

| T [K] | DFT | Experiment | Recursive |
|-------|-----|------------|-----------|
| 5     | 12.63 | 12.8 ± 0.2 | 12.07     |
| 80    | 12.65 | 13.0 ± 0.3 | 12.08     |
| 100   | 12.66 | 13.4 ± 0.3 | 12.10     |
| 250   | 12.85 | 13.4 ± 0.2 | 12.46     |
| 270   | 12.91 | 12.54      |           |

In order to assess the relative contributions of vibrational, translational and librational contributions to carbon kinetic energies in solid C\textsubscript{60}, in what follows we will resort to the model
of the nuclear kinetic energy for a nucleus in a molecular crystal, introduced by Colognesi et al. [10,11]. It is worth noting that the model can be employed in two independent routes:

- In the first route, all components of the S-T tensor, $R_{ij}$, are computed based on the optimised geometry of the molecule obtained from the ab initio calculation, followed by the calculation of the rotationally averaged value $\langle \sigma_{S-T}^2 \rangle$ from Eq. 5;
- In the second route, the rotationally averaged contribution due to internal vibrations, $\langle \sigma_{intra}^2 \rangle$ from Eq. 7, is subtracted from the experimental value of the total second moment obtained from fitting the NMDs using the isotropic Gaussian model, denoted as $\sigma^2$, yielding $\sigma^2 - \langle \sigma_{intra}^2 \rangle$.

Physically, the first route amounts to a classical rigid-body calculation for uncorrelated translational and hindered rotational motions of entire $C_{60}$ molecules. Contrary to the first route, the second one does not assume any uncorrelated rigid body rotation and translation. It assumes, however, the lack of correlation between the intramolecular vibration of carbon nuclei in $C_{60}$ molecules and other modes contributing to the total nuclear kinetic energy of carbon. In the case of the solid $C_{60}$ under investigation, the intramolecular vibration contribution to carbon kinetic energy was obtained based on existing results from a periodic-DFT LD calculation in the CASTEP code obtained, in light of practically dispersion-less phonon spectra, by diagonalisation of dynamical matrices at zero wave-vector (Γ-point-LD calculation) [6].

The STD values of NMDs, resulting from of both routes of calculation performed for the $C_{60}$ as a function of temperature, denoted as $\sqrt{\langle \sigma_{S-T}^2 \rangle}$ and $\sqrt{\sigma^2 - \langle \sigma_{intra}^2 \rangle}$, respectively, are plotted in Fig. 4.

The first striking feature evident in Figure 4 is that the prediction for the sum of the
translation and hindered rotation contributions to the STD of carbon NMD in C_{60}, calculated based on the rigid-body model using the S-T tensor, is systematically lower than the prediction based on the difference between the experimental STD value and the rotationally averaged vibrational contribution, obtained using \textit{ab initio} periodic-DFT approach. In other words, the experiment seems to account for more kinetic energy stored in translations and hindered rotations than the ST model predicts. This significant discrepancy between the results of both routes of the calculation becomes more intuitive in the light of the following remark. The way in which the rigid-body prediction for the nuclear kinetic energy of carbon due to translation and hindered rotation of entire C_{60} molecules is calculated is reminiscent of the Translation-Libration-
Screw-rotation (TLS) model of rigid-body harmonic anisotropic displacement parameters (ADPs), introduced in crystallography by Schomaker and Trueblood [33]. The TLS method has a very well known deficiency. Namely, whereas it is successfully used to predict ADPs of heavy atoms, it is known to fail for the calculation light-atom ADPs based on the extrapolation of heavy-atom ADPs using the librational and translational motion tensors of the same molecule [34,35]. The reason for this failure is that light-atom ADPs depend more on medium-to-high frequency modes. Thus, more sophisticated schemes, including the TLS+ONIOM method, are necessary, as they combine the rigid TLS model with \textit{ab initio} computed estimates of the contribution to ADPs from internal degrees of freedom [35].

However, the LD-inspired approach is likely to fail in the case of lightweight atoms as a result of the classical nature of the treatment of the nuclear degrees of freedom in the \textit{ab initio} simulation, which ignores “non-trivial nuclear quantum effects” [33]. In the end, only path-integral molecular dynamics (PIMD) simulations are capable of capturing these effects, especially at cryogenic temperatures [36]. Moreover, any rigid-body-inspired method, augmented with classical \textit{ab initio} calculations for the vibrational contribution due to internal degrees of freedom in a molecular crystal, will render itself much more useless with respect to the calculation of the shape of an NMDs than it is in the case of the ADP prediction using the TLS. The reason for this relatively larger inaccuracy in the case of the NMD calculation is that, from the point of view of LD, the ADPs can be termed as “minus-first moments of apVDOS”, whereas the widths of NMDs can be termed as “plus-first moments of apVDOS” [3,37]. In consequence, the widths of NMDs are much more sensitive to medium-to-high frequency modes than the values of ADPs. Also, NQEs, including ZPE effects, may constitute another source of systematic errors for the LD-based predictions of NMD widths of lightweight nuclei, similarly as it is in the case of ADP predictions. NQEs have been shown to be important already at room temperature for nuclei as heavy as sulfur [38]. For oxygen, a nucleus one-third heavier than carbon, even at 750 K, the NQE contributions render its kinetic energy ca. 10% higher than the classical mean kinetic energy per atom [39]. Despite the relative importance of NQEs, even for medium-weight nuclei, the fully-pledged PIMD-based modelling of both ADPs and NMDs renders itself very often prohibitively expensive due to the fact that it requires the use of open-path PIMD [40,41]. Even less-accurate but more efficient methodology, based on the path integral generalized Langevin equation thermostat (PIGLET) [42], is beyond the scope of the present study.

However, despite the lack of a PIMD-based prediction, the qualitative appraisal of the dynamical behaviour of \ce{C60} molecules in the solid phase below room temperature, based on results shown in Figure 4, is still possible due to the fact that the NQE contribution to the carbon NMD is expected to be approximately constant over the entire range of temperatures and equal to the value in the limit of zero temperature. This zero-temperature-limit contribution can be assessed by noting that in the limit of zero temperature all rotation and translation of entire \ce{C60} molecules should cease. Moreover, in the limit of zero temperature, the ZPE contribution to the vibrational kinetic energy should be in principle accounted for by the LD-based calculation. Thus, the value of $\Delta \sigma$ obtained in the limit of $T \to 0$ K, equal to $2.25 \pm 0.25$ Å$^{-1}$, should represent an upper conservative bound of NQE contributions to the carbon NMD width. This assessment is further corroborated by the observation that $\Delta \sigma$ is, within one STD, constant between 0 K and 90 K (see red trace and data points in Figure 4).

Encouraged by the argumentation presented in the above paragraph and motivated by the assessment described in the literature [5], one can attempt to perform an appraisal of the structural behaviour in solid \ce{C60} between 90 K and 260 K in terms of the role played solely by reorientational motion of entire \ce{C60} molecules via hops between two energetically similar configurations corresponding, however, to one local and one global potential energy surface (PES) minimum. The first obvious remark to start with is that a rigid-body calculation, unlike a molecular dynamics-based one, does not explore the potential energy surface (PES) and thus
the NMD widths obtained using the S-T tensor cannot be linked to any PES minima. However, the picture widely accepted in the literature [5] is that at high temperatures, \( T > 260 \) K, \( \text{C}_{60} \) molecules are able to perform nearly isotropic free rotation about their lattice sites. Below 260 K, \( \text{C}_{60} \) rotations are restricted to hops between the two favourable orientational positions. With increasing temperature, the hopping frequency increases while also shifting the population of molecules in the global PES minimum to the local one. David et al. [5] put forward a model of uniaxial reorientation of entire \( \text{C}_{60} \) molecules principally about the (111) direction via 60° hops between two energetically similar configurations that involve the facing of either a pentagon or a hexagon opposite a carbon-carbon double bond of a neighbouring \( \text{C}_{60} \) molecule (designated P and H configurations, respectively). They considered a more appealing description of the reorientation between these two configurations that involves smaller, ca. 36°, hops about the (110) directions that are straddled by carbon-carbon double bonds [5]. In this model, any anticlockwise rotation of ca. -36° about [101] returns the molecule to a new P configuration and any clockwise rotation of ca. 36° along [011] results in a new H configuration. The resultant pseudo-random sequence of uniaxial reorientations has a quasi-isotropic nature when averaged over time, whereby all 60 degenerate P and 60 degenerate H configurations may be accessed [5]. Finally, below 90 K all rotational motion ceases to exist, and the system becomes trapped in a given orientational ordering. Interestingly, there is a kink in the residual value of the carbon NMD width at 90 K, clearly seen in Fig. 4, followed by a linear trend continuing until 260 K, the temperature at which \( \text{C}_{60} \) molecules are able to perform isotropic free rotation about their lattice sites. This kink might signal an onset of the quasi-isotropic hopping motion, described in the model by David [5], that cannot be accounted for within the sample rigid-body S-T-based calculation.

A molecular dynamics simulation of the \( \text{C}_{60} \) crystal lattice in the face-centred-cubic structure under progressively raised pressure was performed by Baumeur et al. [43], to illustrate the limits of the crude pseudo-atom approach and the validity of the potential in the rigid molecule, when seeking for possible phase transitions. Baumeur achieved a good description of \( \text{C}_{60} \) crystal properties using the Cheng and Klein potential in the low-pressure region at 5 K. Furthermore, the carbon apVDOS was worked out from the Fourier transform of the Velocity Auto Correlation Function (VACF). The obtained apVDOS had a peak at 15 cm\(^{-1}\) (1.86 meV). Converting this value to into STDs of carbon NMD, calculated within the isotropic Gaussian NMD model, yields \( \Delta \sigma \) equal to 1.94 Å\(^{-1}\) at 5 K, in very good agreement with values plotted in Figure 4. Thus, one can put the upper bound on the total amount of the nuclear kinetic energy of carbon due to molecular reorientation motion of entire \( \text{C}_{60} \) molecules via hops between two energetically similar configurations at 260 K by assuming that the whole difference between \( \Delta \sigma \) at 260 K and 90 K is due to this type of hopping motion. This assumption yields the kinetic energy of the hopping motion of ca. 6 meV at 260 K. Classical constant-pressure molecular-dynamics simulations using a pairwise-additive atom-atom Lennard-Jones (LJ) potential have been demonstrated to provide an excellent account of the carbon apVDOS, whereas the quality of the reproduction of the librational modes, including the one of the high-temperature rotator phase of both solid \( \text{C}_{60} \) and solid \( \text{C}_{70} \), was demonstrated to be less satisfactory [44, 45]. The librational phonon density of states for a triclinic lattice of solid \( \text{C}_{70} \) at 100 K, calculated using classical molecular dynamics (CMD) approach with a LJ potential [44], peaks at the kinetic energy of ca. 11 cm\(^{-1}\) (1.36 meV), thus corresponding for isotropic Gaussian NMD model, to \( \Delta \sigma \) equal to 1.66 Å\(^{-1}\) above the zero-temperature-limit value of 1.94 Å\(^{-1}\), attributed to translational motion only. Applying a classical rigid-body ST-inspired correction to account for the difference in size of \( \text{C}_{60} \) and \( \text{C}_{70} \) molecules, one comes up with \( \Delta \sigma \) equal to \( \sqrt{\frac{65}{70}} \times 1.66 = 1.54 \) Å\(^{-1}\). Thus, the total carbon NMD width at 100 K should yield \( \sqrt{1.66^2 + 1.94^2} = 2.48 \) Å\(^{-1}\), which is in very good agreement with the \( \Delta \sigma \) calculated from the NCS experiment. On the whole, the classical MD calculations using the LJ potential for the solid \( \text{C}_{60} \) yield satisfactory agreement with experiment. The values
of librational energies lie between 1.3 and 2.5 meV, compared to the observed range of 1.8 to 4.0 meV [45–47]. The bond-charge model proposed by Spirk et al. [48] yields phonon-dispersion curves with the highest energy phonon of 5.3 meV, as compared to the highest value observed experimentally of 6.8 meV, with the calculated librational energies between 0.9 and 2.2 meV. This is also seen in the calculation of the carbon apVDOS at 100 K, which shows a librational peak at ca. 13 cm$^{-1}$ (1.6 meV), as compared to the experimental value of 2.7 meV [48].

On the whole and quite surprisingly, there have not been not many studies in the literature of a detailed characterisation of individual contributions to the nuclear kinetic energy of carbon in solid fullerenes as a function of temperature. NCS offers a novel route in this respect. The procedure proposed here involving the dissection of the total carbon kinetic energy into contributions due to translation, libration, and vibration, leads to results, shown in Figure 4, that account very well for the distinction between the translational and librational modes of solid C$_{60}$ between 5 K and 260 K. The obtained results correctly reproduce the librational contribution and its temperature dependence due to the reorientational motion of entire C$_{60}$ molecules via hops between PES minima between 90 K and 260 K. However, due to the fact, that in many studies, the theoretical predictions of the reorientation motion are based on MD simulations results, no phonon-dispersion relations for translations and librations can be computed. Thus, more detailed LD-based simulations are necessary to provide the benchmarking against the results of INS and NCS experiments. Phonon dispersion curves and the nuclear kinetic energies obtained from such studies could be, in principle, capable of discerning different hopping scenarios. Thus a combination of an INS and NCS experiments, performed over a wide range of temperatures, and contrasted with the results of ab initio predictions, could lead to a better understanding of the role of the hopping motion of entire C$_{60}$ molecules in the progressive dynamical transition of solid C$_{60}$ towards quasi-isotropic rotation above 260 K. Moreover and most importantly, PIMD, or less computationally-demanding PIGLET calculations, could provide a route towards the assessment of the role played by the NQEs in the carbon dynamics in this temperature range. However, the difficulty due to the lack of the full picture of nuclear dynamics in this important carbonaceous system, caused by the challenging computational requirements of the PIMD methodology, creates an opportunity for the geometrical analysis at the nanoscale to provide further insight, as will be demonstrated in the following section.

4. Nuclear kinetic energy and fractal structure of carbonaceous systems

The theoretical difficulties that are faced by the ab initio modelling of dynamical transitions in C$_{60}$, described in the section above, motivate even further to find correlations between the values of the kinetic energy of a given nucleus and the degree of complexity and ordering of the structural motif characterising the surrounding environment felt by this particular nucleus. The overarching aim here is to predict, based on purely geometrical signatures of a given system, the value of the nuclear kinetic energy and avoid the expensive and complicated ab initio simulations altogether. In this spirit, in what follows we will analyse both past and present NCS results on carbon systems. In doing so, we will order them according to the increased geometrical dimension. To this end, motivated by recent methodological advances in materials science at the nanoscale, we will attempt to categorise system properties under study via application of the concept of the Hausdorff fractal Dimension (HD) [49]. HD serves as a measure of the local size of a space, taking into account the distance between its points. For the dimension of fractals, HD is based solely on its properties of scaling and self-similarity, and gives a non-integer result. This concept, widely used in topological analysis in mathematics, is also widely applied in many areas of physical chemistry, with theoretical and experimental studies of diffusion, percolation, phase transitions, bonding to name but a few [50–52].

HD analysis has already been performed successfully in the case of carbon systems at the nanoscale, concretely in the description of conductance fluctuations in high mobility monolayer
graphene [51]. This study is a perfect example of the fact that the HD related to the geometry of the system may, in general be different from the HD attributed to a physical process that takes place in this system. Concretely, for a typical graphene sample fabricated on a SiO$_2$ substrate the authors quote HD of 1.3. However, the Higushi algorithm, applied to compute the HD dimension of conductance fluctuations, yields a HD value of ca. 1.2 at 0 K to ca. 0.8 at 30K [51]. Moreover, unlike its geometrical counterpart, the HD of the conductance fluctuations exhibits a progressive increase for low temperatures. The authors attribute these increase to the fact that the conductance fluctuations are not purely random but have a statistical fractal structure associated with an increase in the complexity of the mechanisms that create them [51]. Above approximately 10 K, they observe a very simple, nearly binary, mechanism, whereas for lower temperatures the fluctuations become more complex approaching the HD of a pure Wiener process (HD = 1.5).

As noticed by Zhang et. al. [52], macroscopic geometrical methods can hardly describe events at the nanoscale and there is an upsurge of studies employing nano-geometry as an effective mathematical tool for exploring nanoscale physical and mechanical phenomena. To this end, the atomic lattice structure of perfect single-layer graphene can actually be regarded as a kind of hierarchical fractal structure [52]. The interplay between geometrical parameters and the properties of graphene has been shown in a number of recent studies. Substrate-induced sub-lattice symmetry breaking, giving rise to energy gaps in electronic structures [53], strain causing spatial modulations in the local conductance [54], local uniform magnetic field creation that exceeds 10 Tesla in magnitude [55], and curvature-induced changes in heat and electrical conductivities [56] are to be mentioned but a few. Contrary to the work of da Cunha et. al. [51], employing the Higushi algorithm, Zhang et. al. [52] found, quite surprisingly, that the outer boundary curve of graphene has a fractal dimension equal to one, quite differently from other normal curves whose fractal dimensions vary from one to two. Moreover, a multi-fractal structure was found comprising a series of strict self-similar hexagons comprised a rotating fractal set slewing at a constant counterclockwise angle of 19.1 degrees when observed from one level to the next higher level. The interior fractal structure was found to have HD of two.

For NQEs, as observed by the NCS, HD analysis may aid the analysis of correlations between the bonding topology and nuclear kinetic energy. To this end, the presented work draws from the pioneering work exploring the use of NCS in the investigation of H$_2$ adsorption in KC$_{24}$, a nanoporous graphite intercalation compound (GIC) [57]. This relatively simple exercise changed the way in which the binding scenarios are portrayed in adsorption studies. Namely, it helped identifying those modes which contribute the most to the binding, as measured relative to completely unbound case of two physically separate systems before the physisorption has taken place.

The link between NCS observables and the HD of graphene can be perhaps best emphasized by first resorting to the HD calculation algorithm. In their work on graphene Zhang et. al. [52] use the mass-radius method, which is based on the relationship of the mass distribution of an object with its radius. The nuclear-mass distribution can be a very good approximation of the graphite HD. Owing to the simple property of the Fourier transform that links position and momentum distribution, the link between NMDs and HD becomes straightforward. As the fractal is constructed by means of step-by-step paving of uniform hexagons, more and more contributions to nuclear kinetic energy of a given nucleus from the nearest and next-nearest neighbours is added. Thus, a natural hierarchical mapping is being established between the geometry of the binding motif and the nuclear kinetic energy involving the same nucleus. Moreover, the dissection of the total nuclear kinetic energy into translations, librations and vibrations adds more degrees of freedom into this mapping. Classically, this mapping is a mere consequence of the the moment of inertia corresponding to a given mass distribution. Quantum mechanically, however, the bonding strength and topology may complicate the picture and render
the self-scaling property of the interaction strength, typical for classical fractal structures, less apparent in practice.

Encouraged by the NCS work on GICs [57] and the success of the HD analysis in graphene, we will proceed to categorise NCS results by the HD dimension starting with a system of the lowest dimensionality in this respect, graphene and its compounds. Nemirovsky et al. [58] have measured the kinetic energy of He atoms adsorbed on activated carbon fibres at sub-monolayer coverage. Even though the authors do not quote any value of the carbon kinetic energy, digitising their data recorded for backscattering detector located at the scattering angle of 142 degrees, shown in Fig. 1 of Ref. [58], and fitting it with a purely Gaussian NMD model yields the carbon NMD width, \( \sigma_C \) of 14.0 \( \pm \) 0.5 Å\(^{-1}\). This value is obtained with relatively large standard deviation error due to the fact that care had to be taken to provide an upper conservative bound for data that was not obtained through the direct recording. Namely, as Nemirovsky et al. point out [58], for the active carbon fibre sample, ACF3000, the surface area was larger than the maximum theoretical limit of a graphite sheet assumed to consist of a single graphene layer adsorbing on its two sides. It was found to be due to the fact that the c-spacing was slightly larger than that of graphite due to lack of alignment of the graphitic layers. ACF pores could thus still be modelled as consisting of three-walled infinite graphitic sheets because the size of the crystallites of graphite are larger than 20 nm and the number of parallel sheets in each crystallite is far larger than that constituting the ACF. Also, it was shown through the analysis of NCS data obtained for He that a small (of the order of few percent) difference in distance between the graphitic layers between pure graphite and the ACF had no influence on the calculated He kinetic energies [58].

The next interesting quasi-2D carbon system investigated by means of the NCS method was the GIC [57]. Geometrically, GICs are characterised by a well-defined composition and regular structure [59,60]. Concretely, in the case of KC\(_{24}\), investigated in the above mentioned work [57], below T=100 K, the system adopts a commensurate \( \sqrt{7} \times \sqrt{7} \) M super-lattice bounded by a higher metal density in the inter-domain regions. These topological constraints have interesting consequences for the magnitude and symmetry of the carbon NMDs obtained from the NCS data analysis. For carbon atoms, the NMD, measured below 5K, exhibited cylindrical symmetry about the c-axis, yet the carbon NMD anisotropy was reversed compared to hydrogen. The value of the carbon NMD width of 13.74 Å\(^{-1}\) for in-plane bonding in the GIC under study was found to be very similar to the experimental value of \( \sim 14.0 \) Å\(^{-1}\), measured by Finkelstein et al. [61] for the base graphite material, registered under the trademark name as Papyex.

Interestingly in the context of the work of Nemirovsky et al. [58] on the ACF carbon, the average carbon out-of-plane width of 8.23 Å\(^{-1}\) in the GIC was significantly smaller than \( \sim 11 \) Å\(^{-1}\) in pristine graphite [57]. Thus, unlike in the ACF the carbon NMD width was found to be quite sensitive to a decrease of the interaction between graphite planes, now separated by 5.6 Å in comparison to 3.35 Å in graphite. Such a reduction in momentum width was rationalised as a consequence of the softening of out-of-plane carbon vibrations by a factor of \((13.74/8.23)^2 \sim 2.8\) and was is in good agreement with Raman data on potassium-doped graphene [62].

The next carbon system to be mentioned in the order of dimensionality progression is C\(_{60}\). This molecule, enjoying almost iconic status in chemistry, has a cage-like fused-ring structure (truncated icosahedron) that resembles a football, made of twenty hexagons and twelve pentagons, with a carbon atom at each vertex of each polygon and a bond along each polygon edge. The closest topological cousin of C\(_{60}\), an icosahedron flake, or Sierpinski icosahedron, is formed by successive flakes of twelve regular icosahedrons. Each flake is formed by placing an icosahedron scaled by \(\frac{1}{\sqrt{1+\phi}}\) in each corner. The HD of C\(_{60}\) is equal to \(\frac{\log 12}{\log (1+\phi)} = \approx 2.5819\).

On the whole, the quantum nature of the chemical binding renders the correlation between the carbon NMD widths and their HD not very clear. This lack of apparent correlation is additionally caused by discrepancies arising in the actual HD values for given systems. These discrepancies
are the consequence of employing different algorithms to compute the HD. Also, sometimes simplifying assumptions are used in the calculations of HD for given physical structures. For example, in fact, C_{60} is a truncated Sierpinski icosahedron and a separate calculation of the HD must be carried out that does not simply use the exact icosahedron symmetry as a starting point. Moreover, different HD calculation algorithms rely on different pattern-recognition methods with different accuracy and image edge detection thresholds.

To avoid problems related to the HD calculation mentioned above, in this work we have calculated the HD using the same computational protocol for all systems under investigation, employing the box-counting method to compute the HD. Box-counting is a method of quantitative image analysis of perimeter roughness, routinely applied in the field of image analysis to characterise the degree of roughness of input images. The box-counting algorithm gives the aggregate perimeter roughness which implies parasitic emission sites for extremely rough perimeters [49]. On the HD scale, a dimension of one equates to a smooth line, while an HD of two implies fractal complexity like that of a Julia set [49]. In other words, in the box-counting method, the number $N$ of boxes of size $R$ needed to cover a fractal set follows a power-law, $N \sim R^{-DF}$, with $DF \leq D$ ($D$ is the dimension of the space, usually $D=1, 2, 3$). Because fullerenes are considered to be categorised as truncated fractals, the fractal dimension calculated for this family of compounds is bound by the above limits, i.e., $1 < H.D. < 2$.

The box-counting algorithm, implemented in Matlab [63], was used here. The algorithm started with an input image to which the Canny algorithm [64] was employed to find the edge within the image and superimposes a grid of $N$ squares over the edge, while counting the number of occupied squares that the edge passes through, $N(s)$. This procedure was continued for an increasing number of squares and the HD was given by the gradient of the logarithm of the number of squares $\log N$, over the number of squares occupied by the edge $\log N(s)$, as indicated by the equation 14:

$$HD = \frac{\log N}{\log N(s)}$$ (14)

In what follows we will present the results of the application of a 3D-variant of the box-count algorithm, employing a protocol that can be summarised in three simple steps. First, the geometry-optimised structure, corresponding to the unit cell used as an input for the ab initio program solving the electronic structure problem and computing apVDOS within DFT, was saved in XYZ format with atomic coordinates expressed in units of Å. Then, a conversion was performed from XYZ format to 3D numeric Matlab variable format. Subsequently, the 3D matrix variable served as input for the 3D box counting variant of the HD calculation algorithm, boxcount [65]. The whole protocol was repeated by adding subsequent unit cells to the initial structure until a given asymptotic size of the super-cell was obtained, for which adding more unit cells to the super-cell did not result in any further change of the HD value.

Applying this algorithm to the individual image of C_{60} yielded, for the case of the C_{60}, HD=2.807. The results of the application of the algorithm are shown in Figure 5. Repeating the above analysis for the case of the GIC system was performed using the original atomic coordinates from the geometry-optimised structure [57], shown in the inset of Figure 6. The HD analysis yielded HD=1.585. Finally, applying the same protocol for the graphene structure in Fig. 7, we obtained HD=1.585, a value slightly above the one obtained using the Higuchi method 1.3 [51].

Our next task, following the HD analysis, was the finding right figures of merit that would support correlations between the HD dimension and NMD shape. Drawing from the experience of the NCS work on cesium hydrogen sulfide [38], the first candidate figure of merit is the Quantum Energy Excess ($QE$), defined as the ratio of spatially averaged nuclear kinetic energy from an NCS experiment, $\frac{3h^2\sigma^2}{2M}$ and its classical counterpart, based on the Maxwell-Boltzmann
Figure 5. The results of the application of the box counting method to calculate the HD of C$_{60}$. See text for details.

Figure 6. The results of the application of the box counting method to calculate the HD of the GIC system, KC$_{24}$. See text for details.
kinetic energy distribution, $\frac{3kT}{2}$

$$\text{QE} = \frac{\hbar^2}{MkT} \frac{\sigma^2}{\sigma_{cl}^2}. \quad (15)$$

As discussed [38], the values of QE of unity provides the limit that corresponds to the situation of no chemical binding of an atom and no many-body correlations present in the system under consideration. Mathematically, this limit can be expressed using the classical limit value of the STD of an NMD, $\sigma_{cl} = \sqrt{MkT/\hbar}$: Consequently, any value of $\sigma$ above $\sigma_{cl}$ and any value of $\text{QE}$ above the classical limit of one, obtained from an NCS experiment, signifies some degree of quantum chemical binding and associated atom confinement in given system under investigation [2,3,37].

Values of $\sigma$ and $\sigma_{cl}$ and QE, calculated for $C_{60}$ at different temperatures, are shown in Table 2. Inspection of the QE values listed in Table 2 leads to the observation that a considerable scattering of QE values across various temperatures is observed. One possible reason behind such scattering of QE values is the fact that QE has been defined as the figure of merit characterising the degree of “quantumness” of a given condensed-matter system by normalising the quantum nuclear kinetic energy measured in an NCS experiment by the value of the corresponding classical counterpart based on the Maxwell-Boltzmann kinetic energy distribution which obeys the classical energy equipartition amongst the classical dimensions in space [38]. The consequence of such definition is that the QE magnitude is simultaneously affected by both the quantum nature of chemical binding and the structural motif characterising the surrounding environment felt by a particular nucleus.

Figure 7. The results of the application of the box counting method to calculate the HD of the graphene. See text for details.
Table 2. First-principles predictions for NMD observables of C in C$_{60}$ at various temperatures. The columns correspond to the classical limit of $\sigma$ and QE, as discussed in the text.

| T [K] | $\sigma$ [Å$^{-1}$] | $\sigma_{cl}$ [Å$^{-1}$] | QE |
|-------|---------------------|-------------------------|-----|
| 5     | 12.63               | 1.112                   | 129 |
| 80    | 12.65               | 4.449                   | 8.08|
| 100   | 12.66               | 4.974                   | 6.48|
| 250   | 12.85               | 7.865                   | 2.67|
| 270   | 12.90               | 8.174                   | 2.49|

Motivated by the fractal dimension analysis presented above, one can introduce a new figure of merit, $\text{QE}_H$, the quantum kinetic energy excess of a given nucleus in a system characterised by a given value of fractal dimension

$$\text{QE}_H = \frac{H D}{3} \frac{\sigma^2}{\sigma_{cl}^2} = \frac{H D}{3} \frac{\hbar^2}{M k T} \sigma^2$$

(16)

In the definition, given by Eq. (16), the factor $HD/3$ provides the necessary normalisation by expressing the quantum energy excess per “effective degree of freedom”. Such normalisation should lead to the smoothing of the correlation between the quantum energy excess and the fractal dimension when comparing a family of condensed matter systems within the same chemical binding motif (for instance, carbonaceous systems characterised by the sp$^2$ C hybridisation, whereby the C atom is attached to 3 groups and so is involved in 3 $\sigma$ bonds).

As the consequence of the introduction of a new figure of merit, $\text{QE}_H$, one can also define a $\text{QE}_H$-derived observable, the STD of NMD normalised by the ’effective degree of freedom’, $\sigma_H$:

$$\sigma_H = \sqrt{\frac{H D}{3} \sigma_{cl}} = \sqrt{\frac{H D \sqrt{M k T}}{\hbar}}$$

(17)

The values of the new figures of merit, $\text{QE}_H$, and $\sigma_H$, are listed in Table 3. One can see that the scaling of $\sigma_{cl}$ and QE, by HD=2.807, leads to a slightly more pronounced quantum character of the carbon momentum distribution in C$_{60}$, especially below 100 K. The reason for this temperature effect is that at cryogenic temperature all motion ceases and the fractal dimension is expected to be dictated only by the system geometry, not the symmetry of the molecular motion. Moreover, the effective system dimensionality is reduced reduced by the HD reflecting the fact that solid C$_{60}$ can be thought of a quasi-2D system of folded 2D sheets. Thus, the nuclear kinetic energy of carbon in solid C$_{60}$ is closer to the value exhibited by a 2D-carbon system like graphene.

On the whole, the calculation of the fractal dimension, HD, for a family of quasi-2D carbonaceous systems, all characterised by the sp$^2$ C hybridisation, proves to be largely insensitive to the degree of complexity and ordering of the structural motif characterising the surrounding environment felt by the carbon. Chemically, this property may be dictated by the presence of strong C=C bonds which largely dominate both the energetics and anisotropy of the bonding. For instance, the fact that in GIC the graphene layers are intercalated with potassium and the hydrogen molecules are pinned, forming a preferential T-shaped geometry with respect to the graphene layers [57] does not seem to change the overall HD of the system markedly. Moreover, in order to corroborate this result, we have re-calculated the HD for graphene layers,
Table 3. First-principles predictions for NMD observables of C in C\textsubscript{60}, $\sigma$, $\sigma_H$, and QE\textsubscript{H}, calculated between 5 K and 270 K. $\sigma_H$ and QE\textsubscript{H} correspond to $\sigma_{cl}$ and QE, scaled by the HD=2.807. See text for further details.

| T [K] | $\sigma$ [Å\textsuperscript{-1}] | $\sigma_H$ [Å\textsuperscript{-1}] | QE\textsubscript{H} |
|-------|-----------------|-----------------|----------------|
| 5     | 12.63           | 1.058           | 142            |
| 80    | 12.65           | 4.233           | 8.93           |
| 100   | 12.66           | 4.732           | 7.16           |
| 250   | 12.85           | 7.482           | 2.95           |
| 270   | 12.90           | 7.776           | 2.75           |

by systematically increasing the lattice spacing along the crystallographic c-axis from the value characteristic of pure graphene to the value which is larger by 20%. The only effect visible was a slight increase in the local maximum (a kink) on the penultimate point in the graph showing the result of the HD calculation, with the asymptotic HD value that remained unchanged. Calculating the QE\textsubscript{H} figure of merit for the ACF graphite system measured by Nemirovsky \textit{et al.} \cite{58} and to those obtained by Finkelstein \textit{et al.} \cite{61} for Papyex, using HD=1.585, we obtain QE\textsubscript{H} of 5.03. The average value of carbon NMD width for the GIC, taking into account in and out of the plane components, yields 12.14 Å\textsuperscript{-1}. However, the GIC measurement was performed at 5 K and thus $\sigma_{cl} = 1.112$ Å\textsuperscript{-1}. This yields the value of QE\textsubscript{H} of 225 for the GIC.

The final carbon structure that remains to be examined is a pure bulk 3D system. As an example of such structure we will take the pyrolytic (oriented) graphite (PG). The PG structure and the HD analysis of it are shown in Figure 8. A value of 13.6 Å\textsuperscript{-1} was obtained by Fielding \textit{et al.} for the PG graphite using NCS at 300 K \cite{21}. Applying the HD renormalisation to carbon NCS data on bulk carbon systems we have to use the HD for the PG, being HD=2. Thus, for the PG we get the value of QE\textsubscript{H} of 3.76.

Having collected figures of merit for a number of carbonaceous systems one has to consider which figure of merit is most sensitive to the fractal dimension. For this, the following remarks are in order. Firstly, the HD changes with temperature. These changes are due to symmetry changes induced by lattice expansion and as well as due to phase transitions.

Moreover and most importantly, however, the effective fractal dimension of a given system is the result of the interplay of the fractal nature of the system geometry and the motion that the system is undergoing at a given temperature. This last remark holds especially in case of random or diffusive motion like Brownian motion or random walk with no self-intersection, calculated to have HD=2 and 1.55, respectively \cite{66}. Practically all types of diffusive motions have their fractal signatures \cite{67}. Thus, the only way to disentangle the motional and geometrical contributions to the fractal dimension is to perform spectroscopic measurements at cryogenic temperature where all classical motion ceases and only ZPE effects are present. Thus, the figure of merit sought for must be temperature-normalised or calculated in the limit of no classical motion. For the same reason, the scaling cannot involve the classical prediction for the widths of NMDs, $\sigma_{cl}$, as it already contains the temperature scaling. Moreover, $\sigma_{cl}$ is only an approximation based on the equipartition theorem. Taking all those constraints into account, let us see if the system fractal dimensionality, expressed via HD, correlates with the QE observable that is normalised by the classical prediction for the quantum nature of the system is getting more pronounced. Inspecting the
values listed in Table 4 one has in mind a picture in which, with increasing number of classical dimensions, subsequent bonds are added to sites, hence increasing the number of ways the kinetic energy of a quantum harmonic oscillator may be distributed over bonds. However, one has to seek an answer to the question how the quantum kinetic energy is redistributed over dimensions, not over bonds, modes or sites. To shed more light on this question, one may note a seminal work on the foundations of mesoscopic quantum physics by David Thouless and collaborators in the context of Anderson localisation \[68,69\]. Thouless showed that any quantum system can be attributed a fundamental energy scale, referred as Thouless energy, \(E_T\) \[70\]. It is a measure of how sensitive the eigenstates in a quantum system are to a change in boundary conditions, thus also a criterion of the degree of quantum localisation of the wavefunctions in the whole system under investigation \[68,70\]. Mathematically, the measure of the localisation, introduced by Thouless, is the participation ratio \(\alpha\) which has its minimum value for a Bloch wave (the participation ratio is unity when all sites participate equally), and has its maximum value, unity, when the wavefunction is completely localized on one site \[68\]. Originally, Thouless applied his theory to wavefunctions describing electrons near the Fermi surface \[68\]. To this end, in an insulator, with localised eigenstates, the \(E_T\) is zero because if the wave functions do not extend to the boundaries their energies will be independent of boundary conditions \[70\]. Furthermore, Thouless showed in his seminal work \[68\] that for the 2D-square lattice the onset of localisation is reasonably sharp, contrary to the case of the diamond lattice where the onset of localization is less sharply defined, and localization occurs less easily than for the square lattice, but more easily than in Andersons theory.

Despite the fact that the Thouless theory was originally developed for electronic states, it can be applied to any eigenstates, including phonons, to characterise the degree of distinction

Figure 8. The results of the application of the box counting method to calculate the HD of the pyrolytic graphene. See text for details.
Table 4. The values of HD and QE calculated for all carbonaceous system considered at T=5 K. See text for further details.

| system    | HD   | QE   |
|-----------|------|------|
| graphene  | 1.3  | 158.4|
| GIC       | 1.585| 120.3|
| C\textsubscript{60} | 2.807| 128.9|
| PG graphene | 2   | 149.7|

between systems with different dimensionality via corresponding apVDOS, $G(\omega)$. For phonons in D dimensions, $G(\omega) \propto \omega^{D-1}$ and $\alpha=1$, as long as the dispersion relation remains linear and only one transverse mode or sub-band is present [70]. However, in case of systems with non-integer fractal dimension, there is always some characteristic length scale which limits the extent of a given system either geometrically, or physically (i.e., a characteristic length scale of spatial correlations along a given dimension). In consequence, this finite length scale introduces effectively a degree of localisation along a given dimension. Drawing from the intuition developed based on the study of the Thouless work on the electronic eigenstates [68] one can expect that this localisation will manifest itself more sharply in systems with HD between 2 and 3 than for bulky 3D systems. Thus, phonon localisation-induced, value of $\alpha<1$, and the effective phonon density of states will scale faster than linear with the dimensionality of a system, as $\frac{D}{\alpha} > D$. In consequence, the first moment of the VDOS and hence the kinetic energy of a given nucleus in the lattice, will grow as $\omega^{\frac{D}{\alpha}}$, thus faster than the dimensionality. Applying a phonon picture one can anticipate that the shorter is the characteristic length scale the more pronounced is the bending of the phonon dispersion relations from a purely linear (acoustic phonon-like) towards more optic phonon-like. The consequence of this dispersion relation bending is the increase of the residual kinetic energy (mode energy in the limit of zero momentum transfer) of extra modes added to the density of states, and thus increase of the first moment of the apVDOS, the nuclear kinetic energy. The net effect of this may be the increased quantum kinetic energy excess in mesoscopic systems with intermediate (HD = 2–3) dimensionality. As mentioned above, the envisaged scaling law may be not universal, i.e., it may be limited to the case of $2 < D < 3$. Moreover, trying to retrieve such relationship from a series of NCS and/or INS measurements may be a difficult task, as the overall trend may be subject to scattering due to system, not the dimensionality-specific diversity. To this end, applying the fractal dimension analysis to the INS and/or NCS results on a series of systems may help in the elucidation of an otherwise barely visible trend, as the fractal dimension-based scale is smoother than an integer-based scale.

5. Summary and Outlook

In this work we have presented a much-needed topological analysis of the nuclear kinetic energy of carbonaceous systems. NMD-inspired figures of merit, computed for a series of historic NCS results on graphene and graphite as well as new results on solid C\textsubscript{60} system, correlate with the topological measure of surface roughness and bending, described quantitatively by the Hausdorff fractal dimension. The main result obtained in this study is that, with decreasing fractal dimensional from nearly 3 towards nearly 1, the quantum nature of the system is being more pronounced. An explanation of this trend is based on the analysis of the localisation of the phonon eigenstates and the consequences of this localisation for the magnitude of the first moment of the atom-projected vibrational density of states, the nuclear kinetic energy. Drawing from the seminal work on eigenstate localisation by Thouless, we conclude that this increased localisation should be manifested more as increased quantum kinetic energy excess
in mesoscopic systems with intermediate (HD = 2–3) dimensionality. This conclusion has very important ramifications for the analysis of the nuclear quantum kinetic energy in a variety of condensed matter systems, including but not limited to, crystals, glasses, alloys, liquids, and, last but not least, biological systems.

Further work is necessary to understand the ramifications of the observed correlations. Topological analysis, aided by fractal-geometry analysis tools, may aid the mapping between the chemical bonding motifs and force matrix symmetry and sparsity, characterising the phonon density of states and hence the nuclear kinetic energy. Such topology-augmented analysis may help to find the smallest geometrical representation of a given system with the smallest number of force constants that can reproduce its vibrational properties within a given precision. In extreme cases of very sparse force constant matrices, extreme speed-up of the LD calculation can be achieved, rendering the \textit{ab initio} calculation utterly unnecessary, as demonstrated by the success of the recursive method of phonon dispersion calculation in solid C\textsubscript{60} system.

Further work on other families of condensed matter systems, chosen to exhibit the same chemical binding motif but different fractal dimensions, may shed more light on the geometrical scaling properties of vibrational densities of states and nuclear kinetic energy and may reveal hitherto unexplored links of these scaling laws to materials properties.

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