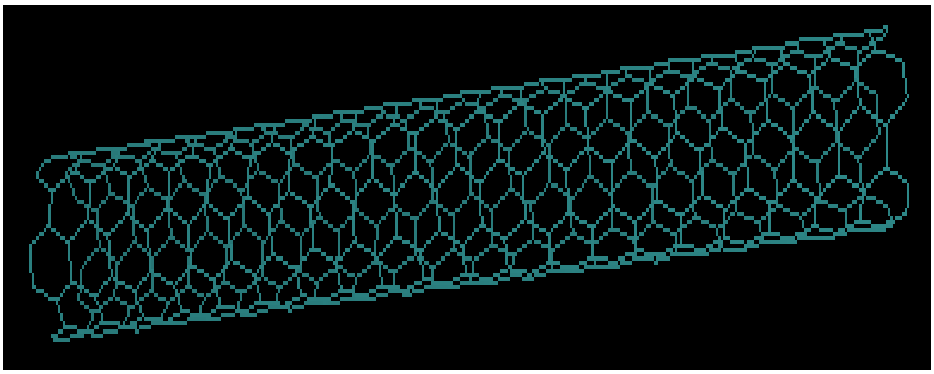
Extraction of Radial Breathing Mode of a Carbon Nanotube using MATLAB



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Acknowledgements

I would like to thank my mentor Dr. Sunita Negi for her constant encouragement, motivation and support without which this project would not have taken its present shape. This project has been a great learning process for me, which has proved to be of immense help in developing my self-belief and confidence of working in the field of carbon nanotubes and nanotechnology.

I would also like to extend my thanks to my faculty members Dr. Shobha Bagai and Dr. Yutheeka Gadhyaan for their help and support in understanding some of the mathematical part of the project and for their valuable suggestions.

Rahul Yadav

Certificate

This is to certify that the report submitted by Rahul Yadav, student of Cluster Innovation Centre, University of Delhi is carried out by him under my supervision as his semester long project. The main aim of this project was to get a hands-on experience with the data analysis technique Singular Value Decomposition (SVD) and to get an exposure to the field of carbon nanotubes.

Although he has completed the work assigned to him satisfactorily, there are some more aspects of this project which could be explored in future.

DR. SUNITA NEGI

ASSISTANT PROFESSOR

CLUSTER INNOVATION CENTRE

Introduction

Carbon nanotubes (CNTs) were first discovered by Iijima. They have now become very important in molecular research because of their potential application for future electrical and mechanical devices. A CNT is basically a tubular structure made up of carbon atoms. This structure is described by a pair of integers (n, m). Depending on these integers (n, m), the tube is characterized as arm-chair, zig-zag, or chiral. The symmetry and electronic properties of a single walled carbon nanotube (SWNT), double walled (DWNT), or multi-walled nanotube. The high tensile strength and strong mechanical properties of these nanotubes make them important for nanomachinary. The knowledge of the normal modes is necessary from the point of view of application of these SWNTs for nanodevices, where excitation at a particular normal mode frequency can give resonance excitation which then be used for extracting useful work from the device. The complex motion of the nanotube when applying certain conditions, can often be resolved into the normal modes of the structure. Hence it is important to develop a good understanding of the normal modes of an SWNT, which forms the subject of our present work. Knowledge of the normal modes can also help suggest methods for "resonantly- driven" nanomotors.

The simplest normal mode, involving in-phase radial movement of the carbon atoms of an SWNT, is called the radial breathing mode (RBM). The RBM frequency is given by $\omega_{RBM} = \frac{A}{d}$, where A is a constant derived experimentally and d is the diameter of the nanotube. Out of all the modes, RBM gives the most intense Raman signal and can be used for nanotube characterization. Thus RBM remained the most widely explored mode for the purpose of nanotube characterization.

In the present work, we study the normal modes of a SWNT using singular value decomposition (SVD) analysis on the MD results. This method offers three advantages. First, it can, in principle, resolve the normal modes of a system in order of the hierarchy, including the associated frequencies as well as spatial distortions. Second, it can handle small as well as large amplitude perturbations

given to the system to excite these modes, i.e., it can identify an-harmonic behavior as well. Third, while the present study only covers SWNTs, it can readily be extended to DWNTs and more complex structures.

Application of SVD for modal analysis

SVD is a powerful technique for solving sets of equations involving matrices that are either singular or numerically close to singular, where methods such as Gaussian elimination or lower-upper (LU) decomposition fail to give satisfactory results. This method can readily be applied to problems where the number of equations is either more or less than the number of unknowns. It is also the method of choice for solving linear least-squares problems. A brief description of SVD is as given under.

Let us consider a physical quality "x" simultaneously measured at "m" different positions (coordinates), and sampled at "n" different times with a sampling interval t_s. The matrix representation of the above observation can be generally expressed by a rectangular array, $x_{ij} = x_j[(i-1)t_s]$, where the row index "i" refers to the coordinate. The SVD of the matrix x_{ij} is expressed as:

$$X = USV^T,$$

Where superscript "T" refers to the transpose of a vector. Here, **U** is an $n \times m$ matrix and **V** is a $m \times m$ square matrix, both of which have orthogonal columns so that $UU^T = VV^T = I$ (identity matrix). **S** is a diagonal matrix, i.e., $S_{ij} = \delta_{ij}s_i$, the quantities $s_{ii} \geq 0$ being called "singular values". The SVD is an analogue of the similarity transformation which diagonalizes a square matrix. The products **SU**

are analogues of the eigenvectors. Therefore $X = USV^T$ is equivalent to the representation $X_{ij} = U_i^k s_k V_j^k$.

The vectors $\boldsymbol{v}^j$, called the principal axes, form an orthonormal basis on which the signal is decomposed. Since the basis diagonalizes the covariance matrix, it can be expected that it describes better the features of the whole signal, compared to other possible bases chosen a *priori*, such as the Fourier basis. This is confirmed by the fact that, in practice, most of the **SU**s are very small compared to a few dominant ones. This explains why SVD is well known in the context of signal processing as noise-filtering technique.

The projections of *X* along **V** (i.e., the product **SU**) are the principal components (PC) of **X.** They give the time evolution of the signal along the corresponding principle axis. This means that the original time series **x(t)** is now described as a sum of time series $x\big((i-1)t_s\big) = \sum_j u_i^j s_j \boldsymbol{v}^j$, each along the new coordinate axis $v^{(j)}$. It is also possible to disregard as noise the components with **SU** below a given level. Since **S** corresponds to singular values, it is justifiable to assume that **U** is a representative of time bases. Only the singular value **S** represents the amplitude of the mode and its variation of **S-** values of different modes as representative of their respective strengths.

A major advantage of SVD analysis is that it separate out modes in descending order of their amplitudes. This means that even fairly weak modes can be identified. Note, however, that for a given initial perturbation, only certain modes may be strong enough to be isolated. If the intention is to study the evolution of a specific spatial mode, the MD simulation can be started to excite that particular distortion in the SWNT, so that that mode becomes stronger.

Conversion of SVD results to get distorted CNT shapes

Each set of three consecutive elements of the **V-** vector corresponds to the change in $x, y,$ and z coordinates of one carbon atom, due to a particular mode. Let $V_{kx}(i), V_{ky}(i)$ and $V_{kz}(i)$ refer to the x, y and z displacements of the ith atom due to the kth mode. We can then write:

$$X_{\text{distorted},i}(t) = \text{Scale}_k(t) * V_{kx}(i) + X_{original,i}\ ,$$

Where $X_{original,i}$ is the x- coordinate of the ith atom before starting the MD simulation, $X_{\text{distorted},i}$ is the distorted x location of the ith atom due to this mode. Similar reactions apply for the y- and z- directions. The scale factor is given by:

$$\text{Scale}_k(t) = U_k(t)S_k\ ,$$

where S_k is the amplitude of the kth mode as yielded by SVD, and U_k is the time series associated with the mode. The combined effects of "N" modes on the ith atom can be obtained by superposition:

$$X_{\text{distorted},i}(t) = \sum_{k=1}^{N} \text{Scale}_k(t) * V_{kx}(i) + X_{original,i}.$$

The distorted positions can be used to compute the time series of average values, e.g., the average radius of a single ring of the SWNT, or the azimuthal rotation of each ring, the axial motion of each ring, and so on.

The type of physical conditions examined in this study

An isolated CNT in a vacuum behaves like a micro- canonical system. This means that it requires NVE simulations, since no energy can flow in or out of the system. A realistic single CNT, on the other hand, would be exposed to a constant pressure and temperature due to interactions with its surroundings. This requires NPT simulations. It is possible that these two conditions could yield a different hierarchy of normal modes. The data used in this study was obtained from an NVE simulation. The significant modes are then extracted using SVD on the given data.

Radial breathing mode (RBM), $m_\theta = 0, m_z = 0$

RBM ($m_\theta = 0, m_z = 0$), the most commonly observed mode in a SWNT involves a uniform (in-phase) expansion and contraction of the entire CNT. In the literature, it is commonly reported as A_{1g} mode. The frequency of this mode is known to vary as $\omega_{RBM} = \frac{A}{d}$.

To excite RBM in an SWNT, $Snegi\ et.\ al$[6] stretched the atomic positions of all the carbon atoms, obtained from NPT relaxation runs, by 5% then run an NVE simulation for 1 ns. They ensure that the atom velocities are set to zero before starting the simulations. A typical set of **S** values, as yielded by SVD, is can be used to plot Amplitude vs Mode number for a (5, 0) SWNT. We also get a similar plot of S values as seen in figure given below.

The use of periodic boundary conditions permits MD simulations with 200 atoms, which yields a maximum of 600 modes from SVD. For this configuration studied, only the first few modes have significant amplitudes. Hence, we are limiting our analysis to the ten most significant modes.

The spatial structure corresponding to the displacement due to the usual in-phase movement of all the carbon atoms of the nanotube in the X-Y plane for mode number can be seen in the **Figure.1**.

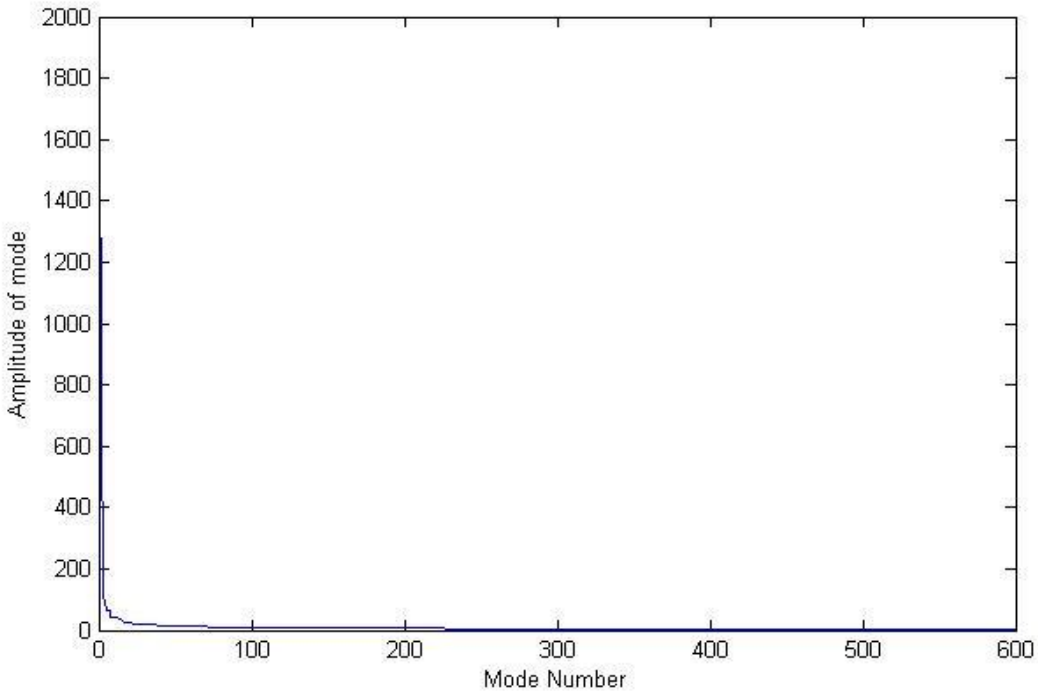

Figure.1. Values of amplitude *S* for all 600 normal modes obtained using SVD analysis of the MD data. Only the first few modes have significant amplitudes.

An SVD code is written in MATLAB to do the above mentioned analysis. We observed mode no. 6 as the radial breathing mode in this case. The spatial structure corresponding to the displacement due to the usual in-phase movement of all the carbon atoms of the nanotube in the X-Y plane for mode number can be seen in the **Figure.2**.

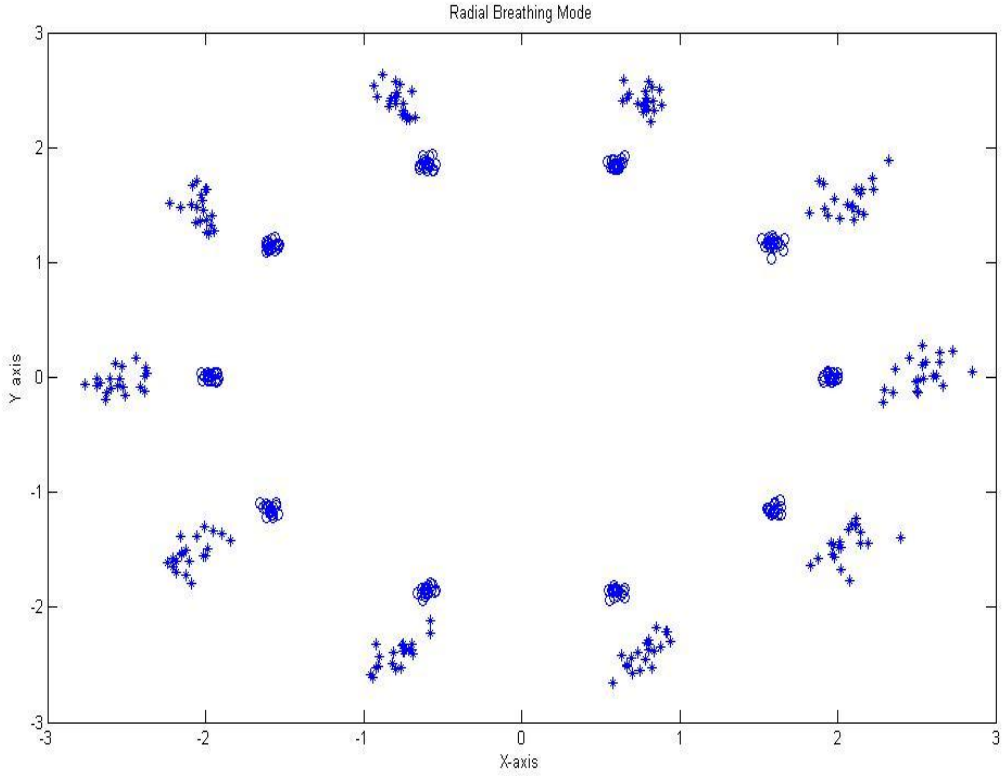

Figure.2- The spatial structure corresponding to the usual in-phase movement of all carbon atoms of the SWNT in the X-Y plane, due to RBM of (5, 0) SWNT. The Z plane lies along the axis of the SWNT.

*The Matlab Code and the Data File are given in the CD with the report.

Conclusion

We have thus extracted normal modes of a single-walled nanotube using SVD analysis on the given molecular dynamics data. The code was written in the Matlab. We could thus extract the usual in-phase motion of the CNT as mode number 6 in this study.

An important aspect of this project would be to extract the frequency corresponding to this radial breathing mode which could then be used for some useful applications of the CNT as reported in the literature.

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Matlab Code

```
%Rahul Yadav - Code for the extraction of Radial
Breathing Mode of CNT.

%Importing the data of the file and conversion of the
data to a matrix
clear all;
fid = fopen('ringall_pos');
n=19840;
for i=1:n
    mtrxnew{i}=textscan(fid,'%f',601);
end
mtrxnew
mtrxnew{1}{1}

for i = 1:n
    mtrx(i,:)= mtrxnew{i}{1};
end
mtrx
initialpos(1,:) = mtrx(1,:);
save f2 initialpos -ASCII
for i = 1:600
    Ex(:,i) = mtrx(:,i)- mean(mtrx(:,i));
end
[U,S,V]=svd(Ex,0);
%Plots
plot(diag(S),'r.')
pause
clf
WW = V.';
ss=diag(S);
save f1 WW -ASCII
save f5 V -ASCII
save f3 ss -ASCII
```

```
%PSD of the first mode:
clf
u1 =U(:,1);



v1 = V(:,1);
[Pxx,F] = psd(u1,19840,1.0e14);
plot(F./3e10,Pxx,'b');
axis([0 1000 0 max(Pxx)]);
legend('U1');
pause
%clf
save fileu1 u1 -ASCII
save filev1 v1 -ASCII
u2 = U(:,2);
v2 = V(:,2);
[Pxx,F] = psd(u2,19840,1.0e14);
plot(F./3e10,Pxx,'b');
axis([0 1000 0 max(Pxx)]);
legend('U2');
save fileu2 u2 -ASCII
save filev2 v2 -ASCII
pause
clf
```