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RESEARCH ARTICLE

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Theoretical treatment of anharmonicity of vibrational modes of single-walled carbon nanotubes

Hengjia Wang[1] | Doyl Dickel[2] | Murray S. Daw[1]

[1]Department of Physics and Astronomy, Clemson University, Clemson, SC 29634, USA

[2]Center for Advanced Vehicular Systems, Mississippi State University, Starkville, MS 39759, USA

Correspondence
Murray S. Daw, Department of Physics and Astronomy, Clemson University, SC 29634, USA.
Email: daw@clemson.edu

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Abstract

We report a computational study, using the "moments method" [Y. Gao and M. Daw, **Modell. Simul. Mater. Sci. Eng. 23** 045002 (2015)], of the anharmonicity of the vibrational modes of single-walled carbon nanotubes. We find that modes with displacements largely within the wall are more anharmonic than modes with dominantly radial character, except for a set of modes that are related to the radial breathing mode that are the most anharmonic of all. We also find that periodicity of the calculation along the tube length does not strongly affect the anharmonicity of the modes but that the tubes with larger diameter show more anharmonicity. Comparison is made with available experiments and other calculations.

KEYWORDS

anharmonicity, carbon nanotubes, moments method, normal modes

1 | INTRODUCTION

Vibrational modes of single-wall carbon nanotubes (SWNTs) are accessible experimentally via Raman spectroscopy.[1–3] A typical Raman spectrum of a SWNT reveals two prominent peaks associated with intrinsic (not defect-related) modes: the radial breathing mode (RBM) and the so-called "G-band," a group of high-frequency modes that have an analog in graphene. Extensive theoretical investigations of the vibrational modes of SWNTs have been carried out, most commonly using the harmonic approximation.[4,5]

By examining the temperature-dependence of the Raman spectra, it is possible to explore the anharmonicity of the RBM and G-band in particular. Raman spectra of the RBM and G-band in SWNT bundles have revealed that their frequency drops with temperature between 300 and 800K.[6,7]. Molecular dynamics calculations on individual SWNTs agree with these observations.[7]

In this work, we apply the "moments method"[8–10] to investigate the temperature-dependence of the frequency of all of the modes of a SWNT. We also study how the chirality, diameter, and length of the tube affect the anharmonicity. We find that generally, all of the vibrational modes shift to lower frequency with increasing temperature. Within that generality, we find that, with respect to anharmonicity, there are three basic groups of modes. Vibrational modes with largely longitudinal character (that is, displacements parallel to the length of the tube) and modes with largely azimuthal displacements (transverse to the length but tangential to the tube) are more anharmonic than the large majority of radial modes. The exception are the azimuthally symmetric radial modes, which are the most anharmonic of all modes. The RBM itself is the most anharmonic of all modes, and the G-band is nearly as much.

In the next section, we discuss the method, and in the following sections, we discuss our results, ending with the conclusions that the RBM is the most anharmonic of the vibrational modes of the SWNT as revealed by its shift with temperature. We also find that the anharmonicity of these modes is not sensitive to chirality or length but does

depend on diameter. We discuss our results in relation to experiments and previous calculations.

2 | METHOD

The moments method is an approximation based on low-order moments of the Liouvillian operator,[8] which is the time-evolution operator of phase-space functions for a *classical* dynamical system. Beginning with the harmonic force constant matrix for the particular cell, the normal modes are found, indexed by wavevector k and branch b. The calculation involves ensemble averaging of products of normal mode amplitudes A_{kb} and accelerations $\ddot{A}_{kb}$, which are obtained by projecting the atomic displacements and forces onto the normal modes. Using the harmonic modes as a basis is justified by the weakly anharmonic character of this system. The lowest, nontrivial moment of the power spectrum of the displacement-displacement autocorrelation

$$\mu_2(kb) = -\frac{\langle A_{kb}\ddot{A}_{kb}\rangle}{\langle A_{kb}^2\rangle - \langle A_{kb}\rangle^2} \tag{1}$$

(where the angle brackets indicate ensemble averages) gives a simple measure of the temperature-dependent dynamics of the system.

The expression in Equation 1 includes the possibility that $\langle A_{kb}\rangle$ is nonzero, which was not included in our previous papers because the systems considered previously had sufficiently high symmetry that the average displacement vanished. However, in the present case, the average displacement of the RBM deviates significantly from zero as the temperature increases, and so we have extended the expressions derived in previous work to include nonzero first moments. The average amplitude $< A_{kb} >$ is defined relative to the equilibrium at T = 0. For most modes, it is 0 but in the case of radial modes, it is not. By this we mean, even when the expansion along the length is allowed, the tube may still be expanded or shrunk in radius compared with zero temperature. It is a kind of thermal expansion/contraction but radially not lengthwise along the tube. It is important to include because the variance around the mean is what allows us to determine the frequency of the mode, and the variance involves both the first and second moments.

The quasi-harmonic (temperature-dependent) frequency $\omega(k)$ is given by

$$\omega(kb) = \sqrt{\mu_2(kb)}. \tag{2}$$

The moment is calculated by standard Monte Carlo integration. This method was used recently to study the anharmonic renormalization of flexural modes in graphene.[11]

In this study, the interatomic interaction is described by a Tersoff potential tailored somewhat for graphene.[12–14] The normal modes are identified from the eigenvectors of the harmonic force constant matrix. The Monte Carlo calculation includes 40,000 steps per atom, which obtains a convergence of all averages to better than 3%.

We generated various tubes of different chirality and length. The usual way[15] to specify the nanotubes is by the chiral indices (n_1, n_2) that describes how a flat graphene sheet can be "rolled-up" to make the nanotube. The diameter is then fixed at $d = \sqrt{n_1^2 + n_1 n_2 + n_2^2}\, a_0/\pi$ where $a_0 = 2.46$ Å corresponds to the second nearest neighbor distance in the surface of the tube. The lattice parameter of the cells is determined for each tube at each temperature by molecular dynamics with adjustable cell size at constant (zero) pressure, thus incorporating thermal expansion or contraction.

As noted above, the RBM is highly symmetrical; the displacements are dominantly radial and are uniform along the length of the tube. Other modes displacing along the radial direction—we refer to simply and more generally as "radial modes"—are related to the RBM by a modulation along the tube axis—as in $\cos(kz)$ where k is the wavevector and z is the distance along the axis of the tube—and/or a phase related to the azimuthal angle ϕ—as in $\cos(m\phi)$ with integer m. The $k = 0$ modes are at the Γ-point in the one-dimensional Brillouin zone. The RBM is then a special radial mode with $m = 0$ and $k = 0$. Most of the radial modes are not visible in Raman spectra but as we have noted before, the RBM appears prominently.

All computational cells are under periodic boundary condition along the length of the tube, and the possible lengths for this periodic condition must be compatible with the chirality. The periodic boundary condition imposed on the tube must then be compatible with the unit periodic length for those chiral indices. For the $(15, 0)$ tube, for example, the unit periodic length is $L_0 = \sqrt{3}a_0$. So the unit cell for the SWNT with that chirality has 60 atoms in it. The actual periodic length $L = nL_0$ must be an integer multiple of this unit periodicity, so that we can simulate tubes with $(15, 0)$ with multiples of 60 atoms.

The periodicity affects the values of the wavevector k that are included in the simulation. That is, for an actual CNT, the values of k are virtually continuous, but for our periodic boundary conditions, the values of k must also be compatible with the periodicity, so that $k = 2\pi Z/L$ where Z is an integer and L is the periodic length, out to the maximum k value in the Brillouin zone of the tube. These discrete values of k are then included in the set of normal modes of the tube with the periodicity imposed. If the periodic length is doubled, for instance, then there are twice as many modes

included, including new k values in between the k values for the smaller cell.

The periodicity is important for two reasons. First, it restricts the normal modes that can be studied in the calculation. So for a tube of a set periodicity, only so many normal modes will occur. Second, the periodicity also restricts the modes that are available to interact with each normal mode. The nonlinearity of the atomic interactions causes a coupling among the normal modes. Thus, the periodicity also restricts the number of modes available for coupling to each normal mode. It is therefore important for us in this work to determine whether the results have converged with respect to the periodic length. We include in our work a study of this convergence.

All together, we studied tubes with lengths ranging from 1.3 to 13 *nm* and diameters from 0.78 to 2.35 *nm*, with various chiralities. In some parts of the analysis, we focus on particular modes, but all have been included in the calculation.

We note additionally that the results we obtain are obviously tied to the Tersoff potential that we have used. The Tersoff potential was devised according to the concept of bond order and contains various prescriptions for angular dependence and also cutoffs that can affect the anharmonicity. One approach that has been used in the literature is to determine explicitly the third- and fourth-order force constants from a potential and to obtain from those the frequency shift. Our approach here is different. We do not go through the intermediate identification of force constants but rather use the ensemble sampling of the correlations among displacements and forces to determine how the anharmonicity connects to the shift in frequency. Because of this, our method can make use of any potential without having to analyze in advance the particular form of a potential.

3 | RESULTS

We begin by presenting the results for a typical nanotube. The anharmonicity is easily displayed by comparing the frequency ω at some temperature as compared with the zero-temperature frequency (ω_0). One measure of the anharmonicity is the ratio $\omega_N \equiv \omega(T)/\omega_0$. This simple measure shows the fractional shift in frequency due to temperature, which is a sign of anharmonicity. It is not the only measure of anharmonicity but it is a simple measure that will allow us to compare the character of modes in a quick way. Figure 1 is a scatterplot of the ratio ω_N versus ω_0 for *all normal modes* of a SWNT(15,0) nanotube with periodic length 6.5 nm (so it has 900 atoms in the unit cell) at $T = 1,200\,K$. As can be seen from the figure, closer analysis shows that the modes fall into three basic groups

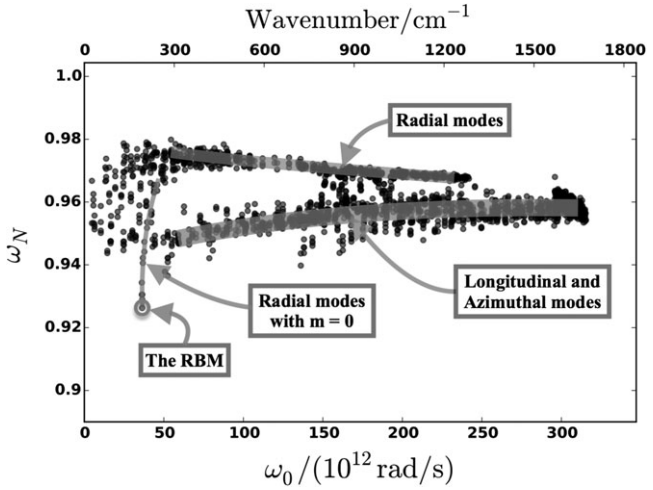

FIGURE 1 Scatterplot of the ratio $\omega_N \equiv \omega/\omega_0$ versus ω_0 for all of the modes of a SWNT(15,0) tube. ω Is the frequency at temperature ($T = 1,200\,K$) and ω_0 is the corresponding harmonic frequency (at $T = 0\,K$). A set of wavenumber labels for horizontal axis is added for more convenient comparison with experiments. For a perfectly harmonic system, all points would be at the top (at a value of 1); due to anharmonicity, all of the modes of this system drop to lower frequency with increasing temperature. The more anharmonic modes exhibit lower values of ω_N. Lines are drawn in this figure as guides to the eye to indicate the different groupings of modes described in the text. RBM = radial breathing mode; SWNT = single-wall carbon nanotube

according to anharmonicity. The least anharmonic modes (those that show the least drop in frequency with increasing temperature) are the radial modes (except for a small group that will be discussed in a moment). The modes with largely longitudinal and azimuthal displacements are more anharmonic. The modes with displacements mostly in-plane seem to be more anharmonic because displacements in the plane will have a more direct effect on the bond length than out-of-plane displacements.

Finally, in Figure 1, there is a standout set at a frequency of about 35×10^{12} rad/s, which are radial modes that are azimuthally symmetric (that is, have $m = 0$). Among this set, we find that the RBM is the most anharmonic of all of the modes of the nanotube. This is consistent with experimental Raman results,[7] where both the RBM feature and the G-band are seen to shift with temperature but in fractional terms, the RBM is more anharmonic. These azimuthally symmetric radial modes differ from the RBM by the wavevector k. So we focus in this work on the RBM modes by showing the temperature-dependent dispersion curves in Figure 2. At $T = 0\,K$, the frequencies (purely harmonic) follow a quartic dispersion

$$\omega(k) = c_0 + c_1 k^4. \tag{3}$$

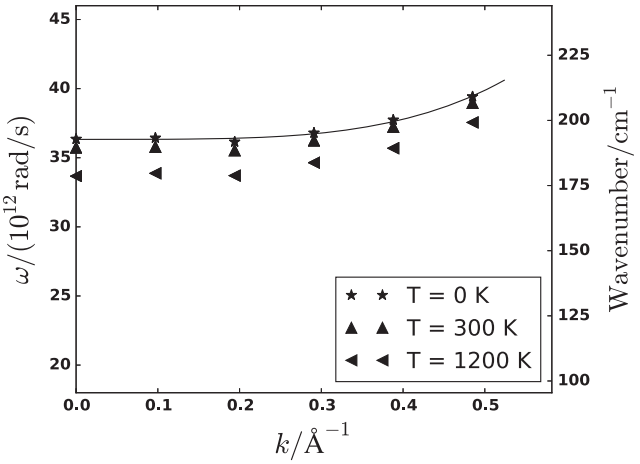

FIGURE 2 The dispersion relation of the azimuthally symmetric (that is, $m = 0$), radial modes of SWNT(15,0) at various temperatures calculated using the moments method. The periodic length is 6.5 nm, so there are 900 atoms in the unit cell. A fit to Equation 3 is shown. The results for several other intermediate temperatures have been calculated and are intermediate to these results, so they have been omitted from this plot for the sake of presentation. SWNT = single-wall carbon nanotube

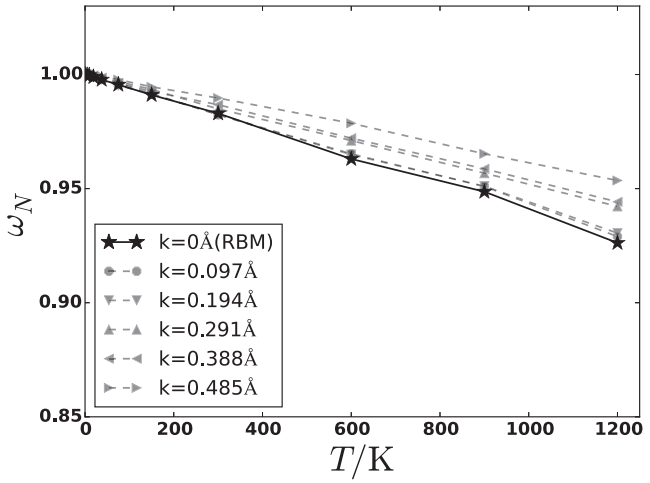

FIGURE 3 The ratio of anharmonic frequency to harmonic frequency ($\omega_N(T) = \omega(T)/\omega_0$) versus temperature for radial modes of various wavevector k. RBM = radial breathing mode

Our values of c_0 and c_1 are 36.3 and 56.9×10^{12} *rad/sec*, respectively (or 193 and 302 for wavenumbers). The temperature dependence is made clearer in Figure 3 by replotting the same data in terms of the ratio to the harmonic frequency versus temperature. In both figures, it is clear that the RBM has stronger temperature dependence than the other azimuthally symmetric radial modes. The frequency of the RBM is roughly linear with temperature, and the temperature coefficient p in

$$\omega_N(T) = 1 + pT \tag{4}$$

is determined for this tube to be $-6\times10^{-5}K^{-1}$. Figure 3 also shows that the absolute value of p decreases with increasing wavevector k. The RBM is the most anharmonic of the set (indeed, of all modes).

Two different experimental observations using Raman spectra of nanotube powders[6,7] of similar diameter (both estimated to be 1.3 to 1.4 nm) determine a slope in the range of 300–800 K of $-7 \times 10^{-5}K^{-1}$ and $-2 \times 10^{-5}K^{-1}$, which span our value. We note that it is not clear how to compare calculations of isolated nanotubes with the experimental Raman spectra of nanotube powders; it is expected that in such powders, the tubes touch and interactions with neighboring tubes would affect their vibrational characteristics. This could be studied theoretically by bringing tubes in contact with each other, which is beyond the scope of the present calculation, but could be done in the future with the same methods.

A molecular dynamics simulation[7] using one of the original Tersoff potentials for carbon[12] for a (10,10) tube (1.4 nm) reported a value of p of $-5 \times 10^{-5}K^{-1}$ very close to our calculation and also within the range reported in the two experiments. The minor difference between the present calculations and those previously reported might be attributed in part to the different chiralities and diameters considered, in part to the interatomic potential (we used a potential with Tersoff form that was somewhat optimized to graphene[14]), or possibly in part to the difference in technique (molecular dynamics vs. moments). At any rate, the differences are not large.

One might hypothesize that the RBM is more anharmonic than other modes because it is radial—that is, maybe displacements in the radial direction are more anharmonic than displacements in other directions—but that is disproved by our results that demonstrate that the large majority of radial modes are not as anharmonic as the RBM. The strong temperature dependence of the RBM frequency, especially in contrast to the other radial modes with $k \neq 0$, can be understood rather in terms of the high symmetry of the RBM (with $k = 0$ and $m = 0$). The RBM has the same symmetry as the nanotube itself (in that any operation that returns the atomic structure of the nanotube to itself also returns the RBM to itself) and can therefore couple easily with other modes. In terms of the usual third-order force constants (see, for example, Madelung[16]), the high symmetry of the RBM allows it to couple with many other modes of the tube. The rotational and translational symmetry of the CNT requires, for example, that the third-order coupling among modes with indices (k_1, m_1), (k_2, m_2), and (k_3, m_3) can be nonzero only if $k_1 + k_2 + k_3$ is an integer multiple of $G = 2\pi/L_0$ and if $m_1 + m_2 + m_3 = 0$. Because the RBM has $k = 0$ and $m = 0$, it can form a third-order coupling with any other (k, m)

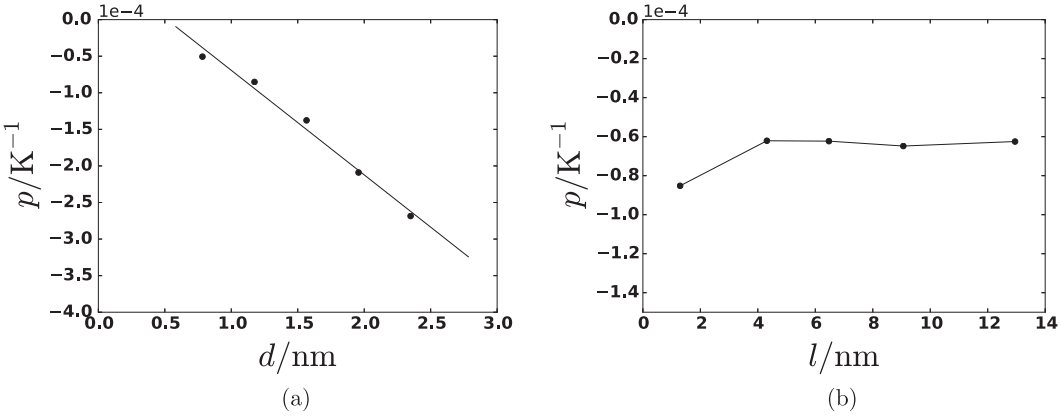

FIGURE 4 In (a), the slope p of the temperature dependence of the frequency (Equation 4) of the RBM is plotted versus the diameter d of the tube. For this plot, we chose a series of tubes with chirality from (10,0) to (30,0). Other corresponding sequences of tubes show similar behavior. In (b), the slope p of the temperature dependence of the frequency (Equation 4) of the RBM of the (15,0) SWNT is plotted versus the periodic length l of the supercell. Tubes of from 3 up to 30 unit lengths are included in this plot. RBM = radial breathing mode

and its symmetry-related partner $(-k, -m)$. This ubiquitous coupling would mean that the frequency shift of the RBM may depend on the number of other modes present in the tube. Because of the periodic boundary condition, the value of k is discrete and the spacing is determined by the number of unit lengths included in the cell. The number of such modes available for coupling will vary with tube diameter and length, so we investigate the possible effect of this in the following.

In Figure 4a, we show that the value of p for the RBM (from Equation 4 and Figure 3) depends on the diameter of the tube. That is, the anharmonicity of the RBM is stronger for tubes with larger diameter. This is consistent with the observation in the previous paragraph, because as the diameter of the tube increases, the number of modes that are available to couple with the RBM increases, thereby resulting in a stronger anharmonicity.

However, by contrast, we show in Figure 4b that the temperature dependence of the modes is not very dependent on the periodic length of our calculation. Periodicity restricts the calculation so that only vibrational modes with wavelength commensurate with the periodic length are allowed. Increasing the length of the periodic cell allows more modes to be present and also to couple with the RBM that is present always. However, our results indicate only a weak dependence of the anharmonicity on the periodic length, so that our conclusions are converged with respect to the periodic boundary condition.

4 | CONCLUSIONS

We have presented the results of a study of anharmonicity of vibrational modes of SWNTs obtained by the "moments method," which is based on Monte Carlo averages of products among displacements and forces. The forces and energies required for the MC calculation were obtained from a semiempirical Tersoff potential, somewhat optimized for graphene.

Generally, all modes shift down in frequency with increasing temperature. Modes with largely in-plane character (longitudinal and azimuthal modes) are more strongly anharmonic than most modes with radial character, with the exception of azimuthally symmetric radial modes (which includes the RBM). In terms of the fractional shift in frequency, the RBM is the most anharmonic of all modes of the nanotube. The temperature dependence of the frequency of the RBM increases with the diameter of the tube. This is attributed to an increase in the number of azimuthal modes eligible to couple with the RBM. As far as we can determine from searching the literature, this is the first time that the effect of diameter on the anharmonicity has been appreciated. The pronounced anharmonicity of the RBM is attributed to its ubiquitous coupling to other azimuthal modes, which is allowed by its high symmetry. The results provide a clearer picture of the anharmonicity of the vibrational modes of a SWNT.

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ORCID

Murray S. Daw http://orcid.org/0000-0003-4725-6460

REFERENCES

[1] H. Hiura, T. W. Ebbesen, K. Tanigaki, *Chem. Phys. Lett.* **1993**, *202*, 509.

[2] M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, *Phys. Rep.* **2005**, *409*, 47.

[3] C. Thomsen, S. Reich, *Top. Appl. Phys.* **2007**, *108*, 115.

[4] P. C. Eklund, J. M. Holden, R. A. Jishi, *Carbon* **1995**, *33*, 959.

[5] M. Aydin, D. Akins, *Vib. Spectrosc.* **2010**, *53*, 163.

[6] H. Li, K. Yue, Z. Lian, Y. Zhan, L. Zhou, S. Zhang, Z. Shi, Z. Gu, B. Liu, R. Yang, H. Yang, G. Zou, Y. Zhang, S. Iijima, *Appl. Phys. Lett.* **2000**, *76*, 2053.

[7] N. Raravikar, P. Keblinski, A. Rao, M. Dresselhaus, L. Schadler, P. Ajayan, *Phys. Rev. B* **2002**, *66*, 235424.

[8] Y. Gao, D. Dickel, D. Harrison, M. Daw, *Comput. Mater. Sci.* **2014**, *89*, 12.

[9] Y. Gao, M. Daw, *Modell. Simul. Mater. Sci. Eng.* **2015**, *23*, 045002.

[10] Based on the moments formalism,[9] a package called *Jazz* was implemented to calculate lifetimes and frequencies of normal modes in anharmonic systems. *Jazz* is a python wrapper for LAMMPS[17] (http://lammps.sandia.gov) and does Monte Carlo averages to give lifetimes and frequencies mode-by-mode. Generally, the package works with any potential available in LAMMPS, and the public version is freely available on the SourceForge website (https://sourceforge.net/projects/jazzforlammps).

[11] H. Wang, M. Daw, *Phys. Rev. B* **2016**, *94*, 155434.

[12] J. Tersoff, *Phys. Rev. Lett.* **1988**, *61*, 2879.

[13] J. Tersoff, *Phys. Rev. B* **1989**, *39*, 5566. *Erratum:* Phys. Rev. B 1990; 41 3248.

[14] L. Lindsay, D. Broido, *Phys. Rev. B* **2010**, *81*, 205441.

[15] J. Kürti, V. Zólyomi, M. Kertesz, G. Sun, *New J. Phys.* **2003**, *5*, 125.

[16] O. Madelung, (B. Taylor, translator), *Introd. solid state phys.*, Springer, New York **1978**.

[17] S. Plimpton, *J. Comput. Phys.* **1995**, *117*, 1.

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