

# Comment on “Temperature dependence of atomic vibrations in mono-layer graphene” [J. Appl. Phys. 118, 074302 (2015)]

Cite as: J. Appl. Phys. **119**, 066101 (2016); <https://doi.org/10.1063/1.4941385>

Submitted: 18 November 2015 . Accepted: 21 January 2016 . Published Online: 08 February 2016

T. Susi , and J. Kotakoski



View Online



Export Citation



CrossMark

## ARTICLES YOU MAY BE INTERESTED IN

[Temperature dependence of atomic vibrations in mono-layer graphene](#)

Journal of Applied Physics **118**, 074302 (2015); <https://doi.org/10.1063/1.4928324>

[Response to “Comment on ‘Temperature dependence of atomic vibrations in mono-layer graphene’” \[J. Appl. Phys. 119, 066101 \(2016\)\]](#)

Journal of Applied Physics **119**, 066102 (2016); <https://doi.org/10.1063/1.4941386>

[Erratum: “Temperature dependence of atomic vibrations in mono-layer graphene” \[J. Appl. Phys. 118, 074302 \(2015\)\]](#)

Journal of Applied Physics **118**, 159902 (2015); <https://doi.org/10.1063/1.4933377>

## Ultra High Performance SDD Detectors



# Comment on “Temperature dependence of atomic vibrations in mono-layer graphene” [J. Appl. Phys. **118**, 074302 (2015)]

T. Susi<sup>a)</sup> and J. Kotakoski

Faculty of Physics, University of Vienna, Boltzmannngasse 5, 1090 Vienna, Austria

(Received 18 November 2015; accepted 21 January 2016; published online 8 February 2016)

In an interesting recent study [Allen *et al.*, J. Appl. Phys. **118**, 074302 (2015)] (see also their Erratum [Allen *et al.*, J. Appl. Phys. **118**, 159902 (2015)]), Allen and co-workers measured the mean square amplitudes of graphene lattice vibrations between 100 and 1300 K and used a simplified theoretical approximation for the acoustic phonon modes to evaluate the maximum phonon wavelengths supported by the lattice. By fitting their data using the smallest wave-vector as the fitting parameter, they found this to be significantly smaller than the physical size of the graphene crystallites. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4941385>]

In addition to amending the simplified analysis of Allen *et al.*,<sup>1,2</sup> in this comment, we suggest that using an accurate model of the density of states (DOS) for the out-of-plane modes in graphene, for example, as calculated by Tewary and Yang (Fig. 1 in Ref. 3; reproduced as our Fig. 1(a)), could help shed light on this discrepancy. The complete treatment of this problem, including the evaluation of the phonon DOS through calculating the eigenvalues of the dynamical matrix at a large number of points in the Brillouin zone, is beyond the scope of this comment. Instead, we limit here our treatment to available literature data in order to gauge the direction and magnitude of this correction for the out-of-plane acoustic ZA mode.

We have evaluated the ZA contribution by simply integrating the out-of-plane phonon DOS to the highest ZA energy, since in graphene this is equal to the lowest ZO energy. This energy is approximately 85 meV,<sup>4</sup> corresponding to  $\omega_{\max} = 1.29 \times 10^{14} \text{ s}^{-1}$  (Fig. 1(a)). This way we can make a direct comparison to the model used by Allen *et al.*, which is by definition only valid for the acoustic modes. Note that the  $\omega_{\max}$  is not the same as the “Debye frequency”  $\omega_{\text{mZ}}$  for out-of-plane phonons, as defined by Tewary and Yang,<sup>3</sup> because the optical mode ZO is not included here. (Note that in the model by Allen *et al.*, the integral is carried out until  $\omega_{\text{mZ}}$ , but only one phonon mode is assumed.)

The mean square displacement can be calculated as a thermal average of the squared modulus of the second quantization displacement operator<sup>5</sup>

$$\langle \hat{u}^2 \rangle = \langle \hat{u} \cdot \hat{u}^* \rangle_{\text{T}} = \frac{\hbar}{2m} \int \frac{1}{\omega} \coth\left(\frac{1}{2} \hbar \omega / k_{\text{B}} T\right) g(\omega) d\omega, \quad (1)$$

where  $g(\omega)$  is the phonon DOS (in the current case, the DOS for the out-of-plane acoustic phonons). (This seems to be missing in the derivation of Allen *et al.* given in their supplementary information. The “density of states  $\sigma$ ” mentioned there is only the normalization term for the DOS; see further.)

In principle, a DOS calculated with any approximation can be used here. For example, following Allen *et al.*, we

can use the dispersion  $\omega(k) \sim \alpha k^2$ , where  $\alpha = 6.2 \times 10^{-7} \text{ m}^2/\text{s}$  is obtained<sup>6</sup> through fitting the ZA dispersion near  $\Gamma$ . From this, it is straightforward to derive an approximate 2D density of states as a function of frequency as

$$g(k) dk = \frac{4\pi}{k_{\text{D}}^2} \frac{k}{2\pi} dk \xrightarrow{\omega \sim \alpha k^2} g(\omega) d\omega = \frac{6\pi \alpha^{3/2}}{\omega_{\text{mZ}}^{3/2}} \frac{\sqrt{\omega}}{4\pi \alpha^{3/2}} d\omega = \frac{3}{2} \omega_{\text{mZ}}^{-3/2} \sqrt{\omega} d\omega, \quad (2)$$

where  $k_{\text{D}} = 1.65 \times 10^{-10} \text{ m}^{-1}$  is the wave vector corresponding to the highest out-of-plane phonon frequency  $\omega_{\text{mZ}}$  in graphene, and the prefactors ensure the correct normalization of  $g$  (Fig. 1(a)). As described above, since the treatment is limited to ZA, instead of  $\omega_{\text{mZ}}$ , we use  $\omega_{\max}$  in the following. Inserting this into (2) and the resulting density into (1) leads to the mean-square displacement

$$\langle \hat{u}^2 \rangle_{\text{ZA}} = \frac{3\hbar}{4m\omega_{\max}^{3/2}} \int_{\omega_{\min}}^{\omega_{\max}} \frac{1}{\sqrt{\omega}} \coth\left(\frac{1}{2} \hbar \omega / k_{\text{B}} T\right) d\omega. \quad (3)$$

Using the identity  $\frac{1}{2} \coth(x/2) = \frac{1}{2} + 1/(\exp(x) - 1)$ , we see that this corresponds to, but differs from, the model of Allen *et al.* (Equation (7) in Ref. 1) due to the density of states term in (1). Fitting their data (Fig. 7 in Ref. 1) using (3), we obtain a minimum frequency of  $8.3 \times 10^{11} \text{ s}^{-1}$ . Inverting the approximate quadratic dispersion relation, we can express the wavelength as a function of the frequency as

$$\omega(k) \sim \alpha k^2 = \alpha \frac{4\pi^2}{\lambda^2} \Rightarrow \lambda \sim 2\pi \sqrt{\frac{\alpha}{\omega}}. \quad (4)$$

This gives  $\lambda_{\min} = 5.4 \times 10^{-9} \text{ m}$ , which is close to  $2.5 \times 10^{-9} \text{ m}$ , the value originally obtained by Allen *et al.*

However, we can equally well insert into (1) the better-motivated out-of-plane phonon DOS published by Tewary and Yang<sup>3</sup> (Fig. 1(a)), which yields  $\omega_{\min} = 5.9 \times 10^8 \text{ s}^{-1}$ . If we assume that the dispersion relation is still valid (as it should be for low frequencies in the case of acoustic phonons), this corresponds to a wavelength of  $\lambda_{\min} = 6.4 \times 10^{-8} \text{ m}$ , which is about 25 times larger than that obtained by Allen

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: [toma.susi@univie.ac.at](mailto:toma.susi@univie.ac.at).

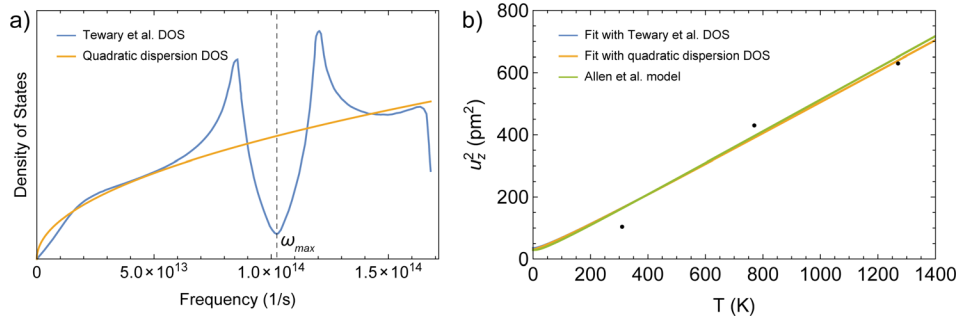


FIG. 1. (a) Out-of-plane phonon density of states from Tewary and Yang<sup>3</sup> and as calculated using the approximate 2D dispersion (Eq. (2)). (b) The out-of-plane mean-square displacements measured by Allen *et al.* (dots) fitted with Eq. (3), including their original fit. Notice that the curves are so close to each other that they are difficult to distinguish from this plot.

*et al.*, while the fit to the data remains equally good (Fig. 1(b)). While still small, this suggests that this surprising finding by Allen *et al.* may be partly due to the limitations within the used approximations.

Based on this quick analysis, it appears to us that a more complete theoretical treatment of the problem, including both acoustic and optical phonon modes as well as the in-plane and out-of-plane vibrations, would be worth its own separate study.

We acknowledge funding from the Austrian Science Fund (FWF) project P 28322-N36 and the Wiener Wissenschafts-,

Forschungs- und Technologiefonds (WWTF) project MA14-009.

<sup>1</sup>C. S. Allen, E. Liberti, J. S. Kim, Q. Xu, Y. Fan *et al.*, *J. Appl. Phys.* **118**, 074302 (2015).

<sup>2</sup>C. S. Allen, E. Liberti, J. S. Kim, Q. Xu, Y. Fan *et al.*, *J. Appl. Phys.* **118**, 159902 (2015).

<sup>3</sup>V. K. Tewary and B. Yang, *Phys. Rev. B* **79**(12), 125416 (2009).

<sup>4</sup>V. K. Tewary and B. Yang, *Phys. Rev. B* **79**(7), 075442 (2009).

<sup>5</sup>Y.-L. Chen and D.-P. Yang, in *Mössbauer Effect in Lattice Dynamics* (Wiley-VCH Verlag GmbH & Co., 2007), p. 177.

<sup>6</sup>E. Pop, V. Varshney, and A. K. Roy, *MRS Bull.* **37**(12), 1273 (2012).