PHONON DISPERSION OF GRAPHENE REVISITED

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The phonon dispersion of graphene is derived by using a simple mass spring model and considering up to the first, second, third, and fourth nearest-neighbor interactions. The results obtained from different nearest-neighbor interactions are compared and it is shown that the k^2 dependence for the out-of-plane transverse acoustic mode obtained in other sophisticated methods as well as experiment occurs only after considering the fourth nearest-neighbor interaction.

1. INTRODUCTION

Graphene, a two-dimensional sheet of graphite and the basis to obtain carbon nanotubes (CNTs), which is of great interest for the current researchers [1–5], is becoming a crucial area of research now. The ongoing research on the vibrational spectrum of CNTs has reopened the research for the vibrational spectrum of graphite as well as graphene. Although the phonon dispersion of graphene has been derived by using several sophisticated methods, the main objective of this paper is to reproduce the same result via a simpler method. We calculate the phonon dispersion of a graphene sheet by using the simple mass spring model of lattice vibrations and considering the interactions up to the first, second, third, and fourth nearest neighbors.

The paper is organized as follows. Section 2 discusses the phonon dispersion relation for a graphene sheet, derived by considering a simple mass spring model. The paper is concluded in Sec. 3.

2. PHONON DISPERSION OF GRAPHENE

Phonon dispersion of graphene has been revisited by researchers in the field because CNTs hold enormous promise in device applications. Several models have been proposed [6–8] to calculate phonon dispersion of graphite as well as graphene. Here, we use the mass spring model [9, 10], in which carbon atoms are
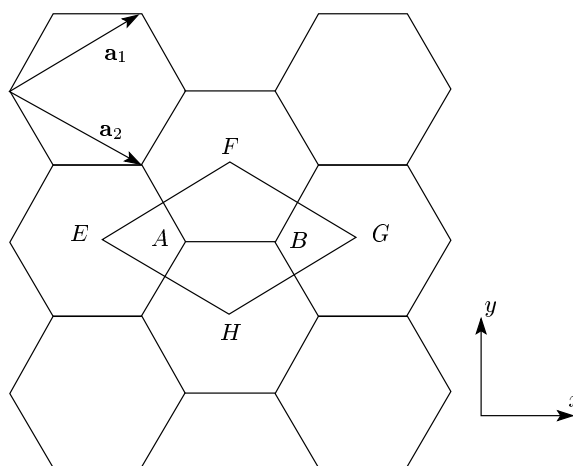

Fig. 1. Unit cell and basis vectors of a graphene sheet

considered to be connected by massless springs with empirically determined spring constants. We systematically do the calculations, including interactions up to the fourth nearest neighbor, and study how the dispersion is affected as more and more neighbors are included in the interaction. We go as far as the fourth nearest-neighbor interaction, because the quadratic dependence of ω on the wave vector k near the origin, for the out-of-plane transverse acoustic mode, which is present in experimental results as well as other more sophisticated theoretical calculations, turns out to appear only when the fourth nearest-neighbor interaction is included. We also compare the phonon spectra obtained from different nearest-neighbor interactions with
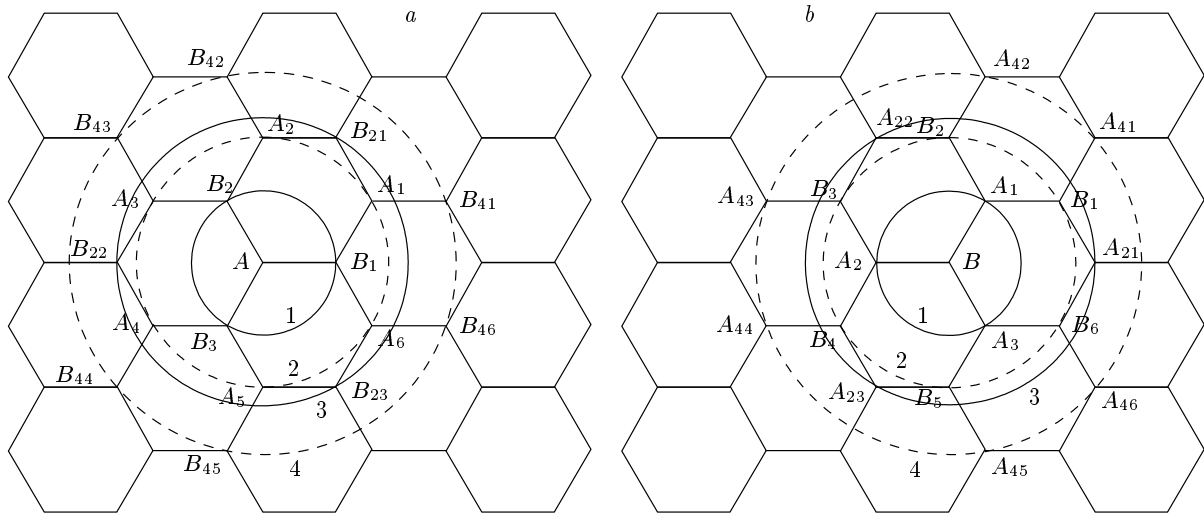
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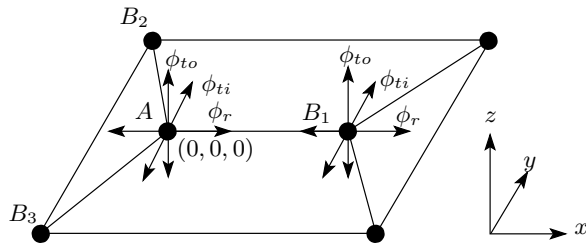**Fig. 2.** Different nearest neighbors for atoms A (a) and B (b)

Fig. 3. Directions of vibrations

ab-initio calculations available in the literature [6], and draw certain conclusions regarding the viability of the simpler spring mass model.

Figure 1 shows a graphene sheet with basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. The atoms A and B (shown inside the rectangle) form the basis set for graphene. In graphene, each atom in the unit cell is surrounded by three first nearest neighbors of the opposite type, six second nearest neighbors of the same type, three third nearest neighbors of the opposite type, and six fourth nearest neighbors of the opposite type. In Fig. 2, these nearest-neighbor atoms are shown by connecting through circles 1 to 4 respectively.

Considering only the first nearest-neighbor interaction, the dynamical matrix for both atoms has been derived from the corresponding equations of motion. Displacements of atoms A and B due to lattice vibration are denoted by u and v, respectively. The position vectors are given in terms of the basis vectors. We con-

sider a lattice site at (r, s) i.e., at $r\mathbf{a}_1 + s\mathbf{a}_2$, where r and s are integers. The separation between A and B atoms at same lattice site is $(\mathbf{a}_1 + \mathbf{a}_2)/3$. Referring to Fig. 2 and considering only the first nearest-neighbor interaction, we write the equations of motion for both atoms as

$$M\frac{d^2 u_{rs}}{dt^2} = C_1(v_{rs} - u_{rs}) + C_2(v_{r,s-1} - u_{rs}) +$$

$$+ C_3(v_{r-1,s} - u_{rs}), \quad (1)$$

$$M\frac{d^2 v_{rs}}{dt^2} = C_1(u_{rs} - v_{rs}) + C_2(u_{r,s+1} - v_{rs}) +$$

$$+ C_3(u_{r+1,s} - v_{rs}), \quad (2)$$

where M is the mass of a carbon atom, C_1, C_2, and C_3 are force constant tensors, and the displacements are

$$u_{rs} = u \exp\left[i\mathbf{k} \cdot (r\mathbf{a}_1 + s\mathbf{a}_2)\right] \exp(-i\omega t),$$

$$v_{rs} = v \exp\left[i\mathbf{k} \cdot (r\mathbf{a}_1 + s\mathbf{a}_2)\right] \times$$

$$\times \exp\left[i\mathbf{k} \cdot (\mathbf{a}_1 + \mathbf{a}_2)/3\right] \exp(-i\omega t).$$

Using these in Eqs. (1) and (2), we obtain the dynamical matrix for graphene:
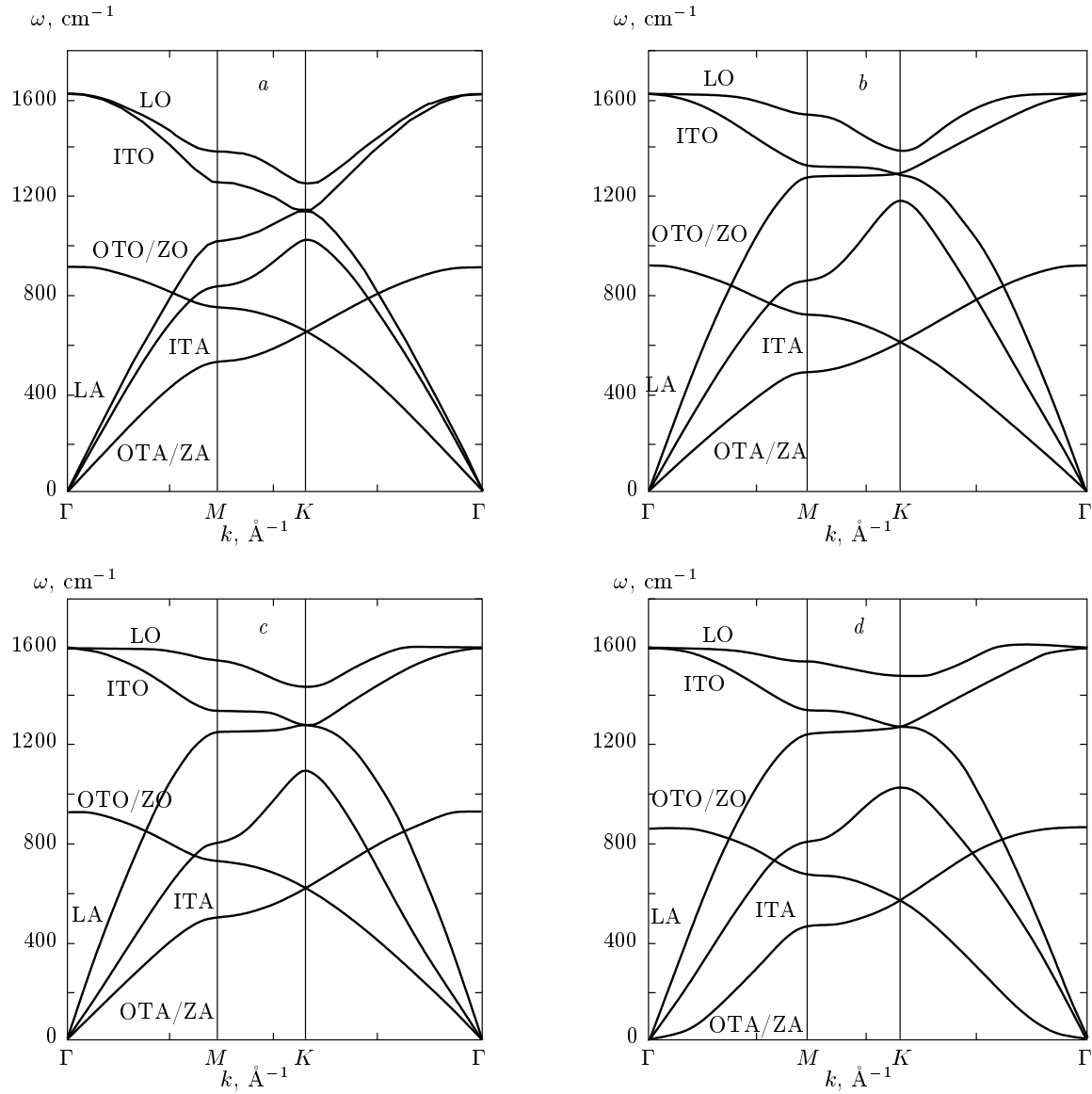
Fig. 4. Phonon dispersion of graphene considering the first (a), second (b), third (c), and fourth (d) nearest-neighbor interactions

$$D =$$

$$= \begin{pmatrix} -M\omega^2 + C_1 + & -\exp\left[\dfrac{i}{3}\mathbf{k}\cdot(\mathbf{a}_1+\mathbf{a}_2)\right] \times \\ +C_2 + C_3 & \times\,[C_1+C_2\exp(-i\mathbf{k}\cdot\mathbf{a}_2)+ \\ & +\,C_3\exp(-i\mathbf{k}\cdot\mathbf{a}_1)] \\ -\exp\left[\dfrac{i}{3}\mathbf{k}\cdot(\mathbf{a}_1+\mathbf{a}_2)\right] \times & -M\omega^2 + C_1 + \\ \times\,[C_1+C_2\exp(i\mathbf{k}\cdot\mathbf{a}_2)+ & +C_2 + C_3 \\ +\,C_3\exp(i\mathbf{k}\cdot\mathbf{a}_1)] & \end{pmatrix}.$$
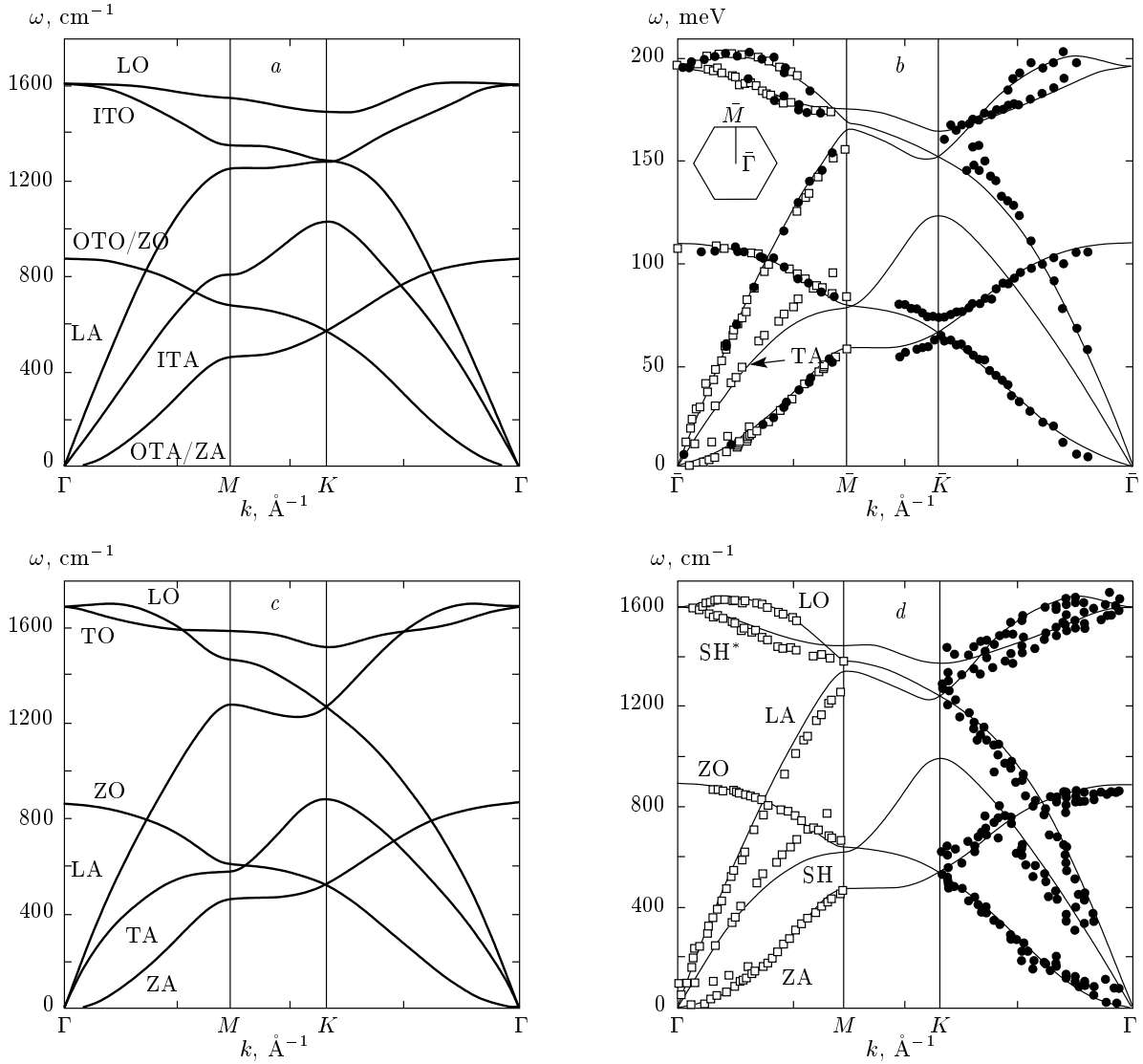
(3)

The matrix C_1 is given by

$$C_1 = \begin{pmatrix} \phi_r^{(1)} & 0 & 0 \\ 0 & \phi_{ti}^{(1)} & 0 \\ 0 & 0 & \phi_{to}^{(1)} \end{pmatrix}, \qquad (4)$$

where $\phi_r^{(1)}$, $\phi_{ti}^{(1)}$, and $\phi_{to}^{(1)}$ are the respective force constants due to the nearest neighbor interactions in the radial, in-plane tangential, and out-of-plane transverse directions. Their values [5] are

$$\phi_r^{(1)} = 36.5\cdot10^4\ \text{dyn/cm}, \quad \phi_{ti}^{(1)} = 24.5\cdot10^4\ \text{dyn/cm},$$

$$\phi_{to}^{(1)} = 9.82\cdot10^4\ \text{dyn/cm}.$$

Fig. 5. Phonon dispersion of graphene obtained from our calculation with the fourth nearest-neighbor interaction (a), and taken from Refs. [8] (b), [6] (c), and [7] (d)

The superscript "1" indicates the first nearest-neighbor interaction. These three directions of vibrations are shown in Fig. 3.

The vibration along the line joining A and B atoms in the graphene plane is the radial vibration, which is along the x-direction. Vibrations along y and z directions are respectively called transverse (tangential) in-plane, and transverse out-of-plane vibrations. Among these three vibrations, there is bond stretching in the radial vibrations and bond bending in the other two vibrations. The other two matrices C_j ($j = 2, 3$) are obtained from C_1 by using the formula $C_j = U_j^{-1} C_1 U_j$,

where U_j is the rotation matrix around the z-direction, which takes atom B_1 to atom B_j. They are given by

$$C_2 = \frac{1}{4} \times$$

$$\times \begin{pmatrix} \phi_r^{(1)} + 3\phi_{ti}^1 & \sqrt{3}\left(\phi_{ti}^{(1)} - \phi_r^{(1)}\right) & 0 \\ \sqrt{3}\left(\phi_{ti}^{(1)} - \phi_r^{(1)}\right) & 3\phi_r^{(1)} + \phi_{ti}^{(1)} & 0 \\ 0 & 0 & 4\phi_{to}^{(1)} \end{pmatrix}, \quad (5)$$

Table. Comparison of our results with other theoretical model and experimental results at different high-symmetry points

Method used to obtain the phonon dispersion	Frequency at the Γ point [cm^{-1}]			Frequency at the M point [cm^{-1}]						Frequency at the K point [cm^{-1}]					
	LO	ITO	OTO	LO	ITO	OTO	LA	ITA	OTA	LO	ITO	OTO	LA	ITA	OTA
Ab initio [6]	1690	1690	860	1580	1475	1280	610	580	460	1520	1260	1260	890	520	520
1st nearest neighbor	1623	1623	920	1389	1259	1025	840	752	532	1256	1147	1149	1029	650	650
2nd nearest neighbor	1623	1623	981	1542	1334	1287	860	720	487	1392	1295	1295	1190	610	610
3rd nearest neighbor	1593	1593	928	1542	1333	1250	803	720	500	1438	1277	1277	1092	615	615
4th nearest neighbor	1603	1603	872	1546	1345	1252	810	673	465	1480	1283	1283	1033	573	573
4th nearest neighbor with a second set of force constant	1605	1605	874	1475	1313	1202	733	703	432	1305	1222	1222	1133	580	580
Experimental [8]	1580	1580	868	1390	1323	1290	630	670	471	1313	1184	1184	—	—	—

$$C_3 = \frac{1}{4} \times$$

$$\times \begin{pmatrix} \phi_r^{(1)} + 3\phi_{ti}^{(1)} & \sqrt{3}\left(\phi_r^{(1)} - \phi_{ti}^{(1)}\right) & 0 \\ \sqrt{3}\left(\phi_r^{(1)} - \phi_{ti}^{(1)}\right) & 3\phi_r^{(1)} + \phi_{ti}^{(1)} & 0 \\ 0 & 0 & 4\phi_{to}^{(1)} \end{pmatrix}. \quad (6)$$

Substituting these matrices in Eq. (3), we obtain a 6×6 dynamical matrix, and setting the determinant of the dynamical matrix equal to zero, we obtain the phonon dispersion relation ($\omega \sim k$) for graphene, which is plotted in Fig. 4a. Because the matrix is 6×6, we obtain six branches for the phonon dispersion. The number six also follows from the fact that there are two atoms per primitive cell, and each atom has three modes of vibration.

Finally solving the eigenvalue equations for the dynamical matrix, we obtain the phonon dispersion relation of graphene [11]. The same procedure is repeated for different nearest-neighbor interactions. The phonon branches for graphene obtained by this method are shown in Fig. 4, which shows that there are three optical and three acoustic branches. The three branches

originating from zero at the Γ point are the three acoustic phonon modes, corresponding to the out-of-plane mode known as the out-of-plane transverse acoustic branch (OTA/ZA), the in-plane tangential (bond-bending) mode known as the in-plane transverse acoustic branch (ITA), and the in-plane radial (bond-stretching) mode known as the longitudinal acoustic branch (LA), listed in order of increasing energy. The remaining three branches correspond to the optical modes: one the nondegenerate out-of-plane mode and two the in-plane modes that remain doubly degenerate as we move away from the Γ point. The three optical branches are called the longitudinal optical (LO), the in-plane transverse optical (ITO), and the out-of-plane transverse optical (OTO/ZO), in the decreasing order of frequency. It is clear from the Fig. 4 that although there are similarities between all the phonon spectra obtained for different nearest-neighbor interactions, with only small quantitative differences, the k^2 dependence for the out-of-plane transverse acoustic branch, obtained in experimental results and other calculations, appears only after including interactions up to the fourth nearest neighbor. Therefore the inter-

actions at least up to fourth nearest neighbors are to be considered for calculating the phonon dispersion of graphene.

The comparison of our results with the results obtained in ab-initio calculations [6], density functional theory calculations [7], and experimental data [8], is shown in Fig. 5. In this figure, plots shown in (a)–(d) are respectively the phonon dispersions obtained in the present calculation, considering up to the fourth nearest-neighbor interaction, experimental data [8], ab-initio calculation [6], and density functional calculation [7].

The open squares and closed circles in Fig. 5d represent experimental data for the phonon dispersion of graphene obtained by different methods described in [7]. In this figure, the authors have mentioned the in-plane transverse acoustic (ITA) branch as Shear horizontal (SH) branch and the in-plane transverse optical as SH*. In Fig. 5b, solid circles and solid curves respectively represent the phonon energy dispersion curves of graphene sheets determined experimentally and theoretically, whereas phonons in the bulk graphite surfaces are shown with open circles for comparison [8]. In Table, to compare the results quantitatively, we have listed the values at high-symmetry points obtained from different nearest-neighbor interaction consideration, those obtained by the ab-initio method, and from experiment [8,12].

3. CONCLUSION

We have obtained the phonon dispersion relation of graphene by using a simple mass spring model and considering up to the fourth nearest-neighbor interaction. We have then compared our results obtained for different nearest-neighbor interactions with experimen-

tal data and with the results obtained by the ab-initio method. The comparison shows that the accuracy is greater as we include more nearest-neighbor interactions and the k^2 dependence, because the out-of-plane transverse mode appears only after considering the fourth nearest-neighbor interaction.

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