

Supplementary Information:
Lattice Dynamics of Graphene Nanoribbons under Twisting

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S1. GENERALIZED BLOCH THEOREM UNDER SCREW SYMMETRY

Under screw symmetry, a twisted structure could be written as,

$$\mathbf{X}_{\lambda,n} = \mathbf{R}^\lambda(\Omega)\mathbf{X}_{0,n} + \lambda\mathbf{T}, \quad (\text{S1})$$

where $\mathbf{X}_{0,n}$ represents the atoms inside the primitive repeating motif. Translation component \mathbf{T} and rotation component \mathbf{R} with twist angle Ω constitute the screw operator $\hat{\mathbf{S}}$. $\mathbf{X}_{\lambda,n}$ is the n^{th} atom inside the replica of the repeating motif screwed λ times by screw operator $\hat{\mathbf{S}}$. To easily show the effect of $\hat{\mathbf{S}}$, we use cylindrical coordinates (r, θ, z) to describe a position vector \mathbf{r} and let z be the screw axis. For an arbitrary function f ,

$$\hat{\mathbf{S}}^\lambda f(r, \theta_0, z_0) = f(r, \theta_0 + \lambda\Omega, z_0 + \lambda|\mathbf{T}|), \quad (\text{S2})$$

where (r, θ_0, z_0) is the initial position vector before the operation of $\hat{\mathbf{S}}$.

The crystal one electron Hamiltonian is,

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}). \quad (\text{S3})$$

The Eq. (S1) indicates that the potential $V(\mathbf{r})$ should also be invariant under helix boundary condition,

$$\hat{\mathbf{S}}^\lambda V(\mathbf{r}) = V(\mathbf{r}). \quad (\text{S4})$$

This means the electronic Hamiltonian $\hat{\mathbf{H}}$ is invariant under screw symmetry. Furthermore, we find

$$\hat{\mathbf{S}}^\lambda \hat{\mathbf{H}} f(r, \theta_0, z_0) = \left[-\frac{\hbar^2}{2m}\nabla_{r, \theta_0 + \lambda\Omega, z_0 + \lambda|\mathbf{T}|}^2 + V(r, \theta_0 + \lambda\Omega, z_0 + \lambda|\mathbf{T}|)\right]f(r, \theta_0 + \lambda\Omega, z_0 + \lambda|\mathbf{T}|) = \hat{\mathbf{H}}\hat{\mathbf{S}}^\lambda f(r, \theta_0, z_0), \quad (\text{S5})$$

which means $\hat{\mathbf{S}}^\lambda$ and $\hat{\mathbf{H}}$ commute with each other. Therefore, these two operators have the same eigenstates. Then we could choose the eigenstate of $\hat{\mathbf{H}}$,

$$\hat{\mathbf{H}}\psi(r, \theta_0, z_0) = E\psi(r, \theta_0, z_0), \quad (\text{S6})$$

which is also the eigenstate of $\hat{\mathbf{S}}$,

$$\hat{\mathbf{S}}\psi(r, \theta_0, z_0) = m\psi(r, \theta_0, z_0). \quad (\text{S7})$$

Note that it is very easy to verify,

$$\hat{\mathbf{S}}^{\lambda_1}\hat{\mathbf{S}}^{\lambda_2}\psi(r, \theta_0, z_0) = \hat{\mathbf{S}}^{\lambda_2}\hat{\mathbf{S}}^{\lambda_1}\psi(r, \theta_0, z_0) = \psi(r, \theta_0 + (\lambda_1 + \lambda_2)\Omega, z_0 + (\lambda_1 + \lambda_2)|\mathbf{T}|) = m^{\lambda_1 + \lambda_2}\psi(r, \theta_0, z_0), \quad (\text{S8})$$

where λ_1 and λ_2 are both integers. Considering Eq. (S8) and helix boundary condition, there should exist an integer ξ , which makes

$$\hat{\mathbf{S}}^\xi\psi(r, \theta_0, z_0) = \psi(r, \theta_0 + \xi\Omega, z_0 + \xi|\mathbf{T}|) = \psi(r, \theta_0, z_0) = m^\xi\psi(r, \theta_0, z_0). \quad (\text{S9})$$

Accordingly, we obtain the eigenvalue of operator $\hat{\mathbf{S}}$, $m = \exp(i2\pi N/\xi)$, where N is an integer. In order to make it convenient for writing, we replace $2\pi N/\xi$ with \tilde{k} and $-\pi < \tilde{k} \leq \pi$. Similar to \tilde{q} for phonon (see manuscript), \tilde{k} can be regarded as helical quantum number for electron. Now we can find the eigenstate ψ satisfies the following relation,

$$\hat{\mathbf{S}}^\lambda\psi(r, \theta_0, z_0) = \psi(r, \theta_0 + \lambda\Omega, z_0 + \lambda|\mathbf{T}|) = \exp(i\tilde{k}\lambda)\psi(r, \theta_0, z_0), \quad (\text{S10})$$

which is the Bloch theory under screw symmetry, *i.e.*, generalized Bloch theorem mentioned in the manuscript.

In the tight-binding approach under translational periodic boundary condition, we could represent ψ by a linear combination of atomic orbitals centered at each atom in a primitive cell. In the case of helix boundary condition, the atomic orbitals could be used as basis functions only when they are rotated to the same orientation with the repeating

primitive motif, which are referred to as symmetry-adapted orbitals. With these symmetry-adapted orbitals as basis, similar to the standard Bloch wave functions, we write the generalized Bloch wave function as,

$$\psi_{n,\alpha}(\tilde{k}, \mathbf{r}) = \frac{1}{\sqrt{2N_h}} \sum_{\lambda=-N_h}^{N_h-1} \exp(i\tilde{k}\lambda) \sum_{\alpha'} O_{\alpha\alpha'}(\lambda\Omega) \varphi_{\alpha'}(\mathbf{r} - \mathbf{X}_{\lambda,n}), \quad (\text{S11})$$

where $\varphi_{\alpha'}(\mathbf{r} - \mathbf{X}_{\lambda,n})$ refers to the local atomic orbital α' on atom n in the primitive cell rotated by λ times. α runs over all the orbitals of single atom and n runs over all the N atoms inside the primitive motif. N_h is an integer, indicating the times of helical operation acting on atomic orbitals. $O_{\alpha\alpha'}$ is the matrix elements of \mathbf{O} , rotating the local atomic orbitals to construct symmetry-adapted basis functions, *i.e.*, $\sum_{\alpha'} O_{\alpha\alpha'}(\lambda\Omega) \varphi_{\alpha'}(\mathbf{r} - \mathbf{X}_{\lambda,n})$. Let z be the screw axis and Eq. (S11) would be more clear in matrix form. For materials only with s and p (p_x, p_y, p_z) orbitals,

$$\begin{bmatrix} \psi_{n,s}(\tilde{k}, \mathbf{r}) \\ \psi_{n,p_x}(\tilde{k}, \mathbf{r}) \\ \psi_{n,p_y}(\tilde{k}, \mathbf{r}) \\ \psi_{n,p_z}(\tilde{k}, \mathbf{r}) \end{bmatrix} = \frac{1}{\sqrt{2N_h}} \sum_{\lambda=-N_h}^{N_h-1} \exp(i\tilde{k}\lambda) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(\lambda\Omega) & -\sin(\lambda\Omega) & 0 \\ 0 & \sin(\lambda\Omega) & \cos(\lambda\Omega) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{bmatrix} \varphi_s(\mathbf{r} - \mathbf{X}_{\lambda,n}) \\ \varphi_{p_x}(\mathbf{r} - \mathbf{X}_{\lambda,n}) \\ \varphi_{p_y}(\mathbf{r} - \mathbf{X}_{\lambda,n}) \\ \varphi_{p_z}(\mathbf{r} - \mathbf{X}_{\lambda,n}) \end{bmatrix}. \quad (\text{S12})$$

For materials with d ($d_{x^2-y^2}, d_{xy}, d_{zx}, d_{yz}, d_{3z^2-r^2}$) orbitals, Eq. (S11) should also contains,

$$\begin{bmatrix} \psi_{n,d_{x^2-y^2}}(\tilde{k}, \mathbf{r}) \\ \psi_{n,d_{xy}}(\tilde{k}, \mathbf{r}) \\ \psi_{n,d_{zx}}(\tilde{k}, \mathbf{r}) \\ \psi_{n,d_{yz}}(\tilde{k}, \mathbf{r}) \\ \psi_{n,d_{3z^2-r^2}}(\tilde{k}, \mathbf{r}) \end{bmatrix} = \frac{1}{\sqrt{2N_h}} \sum_{\lambda=-N_h}^{N_h-1} \exp(i\tilde{k}\lambda) \begin{pmatrix} \cos(2\lambda\Omega) & -\sin(2\lambda\Omega) & 0 & 0 & 0 \\ \sin(2\lambda\Omega) & \cos(2\lambda\Omega) & 0 & 0 & 0 \\ 0 & 0 & \cos(\lambda\Omega) & -\sin(\lambda\Omega) & 0 \\ 0 & 0 & \sin(\lambda\Omega) & \cos(\lambda\Omega) & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{bmatrix} \varphi_{d_{x^2-y^2}}(\mathbf{r} - \mathbf{X}_{\lambda,n}) \\ \varphi_{d_{xy}}(\mathbf{r} - \mathbf{X}_{\lambda,n}) \\ \varphi_{d_{zx}}(\mathbf{r} - \mathbf{X}_{\lambda,n}) \\ \varphi_{d_{yz}}(\mathbf{r} - \mathbf{X}_{\lambda,n}) \\ \varphi_{d_{3z^2-r^2}}(\mathbf{r} - \mathbf{X}_{\lambda,n}) \end{bmatrix}. \quad (\text{S13})$$

As the eigenfunction of $\hat{\mathbf{S}}$ and $\hat{\mathbf{H}}$, $\psi_{n,\alpha}(\tilde{k}, \mathbf{r})$ forms a complete basis set involving only the N atoms in the primitive motif. Now we can write the one-electron wave function Ψ as,

$$\Psi(\tilde{k}, \mathbf{r}) = \sum_{n,\alpha} C_{n,\alpha}(\tilde{k}) \psi_{n,\alpha}(\tilde{k}, \mathbf{r}), \quad (\text{S14})$$

which satisfies the following characteristic equation,

$$\mathbf{H}(\tilde{k}) \cdot \mathbf{C}_m(\tilde{k}) = E_m(\tilde{k}) \mathbf{S}(\tilde{k}) \cdot \mathbf{C}_m(\tilde{k}). \quad (\text{S15})$$

The eigenvector \mathbf{C} in Eq. (S15) is composed of the expansion coefficients C in Eq. (S14). $E_m(\tilde{k})$ denotes electronic energies at a specific helical quantum number \tilde{k} with $m = 1, 2, \dots, N_\alpha$ and N_α is the total number of atomic orbitals in a primitive motif. To solve Eq. (S15), we should also know the elements of Hamiltonian matrix \mathbf{H} and overlap integral matrix \mathbf{S} . The element of Hamiltonian matrix \mathbf{H} is,

$$H_{nn',\alpha\alpha'}(\tilde{k}) = \int \psi_{n,\alpha}^*(\tilde{k}, \mathbf{r}) H \psi_{n',\alpha'}(\tilde{k}, \mathbf{r}) d^3\mathbf{r} = \sum_{\lambda=-N_h}^{N_h-1} \exp(i\tilde{k}\lambda) \sum_{\alpha''} t_{nn',\alpha\alpha''} O_{\alpha''\alpha'}(\lambda\Omega), \quad (\text{S16})$$

where,

$$t_{nn',\alpha\alpha''} = \int \varphi_\alpha^*(\mathbf{r} - \mathbf{X}_{0,n}) H \varphi_{\alpha''}(\mathbf{r} - \mathbf{X}_{\lambda,n'}) d^3\mathbf{r}. \quad (\text{S17})$$

When $n = n'$, $\alpha = \alpha''$, and $\lambda = 0$, $t_{nn',\alpha\alpha''}$ becomes

$$t_{nn,\alpha\alpha} = \int \varphi_\alpha^*(\mathbf{r} - \mathbf{X}_{0,n}) H \varphi_\alpha(\mathbf{r} - \mathbf{X}_{0,n}) d^3\mathbf{r} = \epsilon_{n,\alpha}, \quad (\text{S18})$$

which is the on-site energy of the α orbital of atom n . The element of overlap integral matrix \mathbf{S} is

$$S_{nn',\alpha\alpha'}(\tilde{k}) = \int \psi_{n,\alpha}^*(\tilde{k}, \mathbf{r}) \psi_{n',\alpha'}(\tilde{k}, \mathbf{r}) d^3\mathbf{r} = \sum_{\lambda=-N_h}^{N_h-1} \exp(i\tilde{k}\lambda) \sum_{\alpha''} s_{nn',\alpha\alpha''} O_{\alpha''\alpha'}(\lambda\Omega), \quad (\text{S19})$$

where,

$$s_{nn',\alpha\alpha'} = \int \varphi_{\alpha}^*(\mathbf{r} - \mathbf{X}_{0,n}) \varphi_{\alpha'}(\mathbf{r} - \mathbf{X}_{\lambda,n'}) d^3\mathbf{r}. \quad (\text{S20})$$

When $n = n'$, $\alpha = \alpha'$, and $\lambda = 0$, $s_{nn',\alpha\alpha'}$ becomes

$$s_{nn,\alpha\alpha} = \int \varphi_{\alpha}^*(\mathbf{r} - \mathbf{X}_{0,n}) \varphi_{\alpha}(\mathbf{r} - \mathbf{X}_{0,n}) d^3\mathbf{r} = 1, \quad (\text{S21})$$

indicating the overlap integral between an electron and itself is 1. Up to now, the hopping $t_{nn',\alpha\alpha'}$, on-site energy $\epsilon_{n,\alpha}$ and overlap $s_{nn',\alpha\alpha'}$ of various elements have been parameterized by carrying out first-principles calculation. The quantities of hopping and overlap terms only depend on the distance between atoms at $\mathbf{X}_{0,n}$ and $\mathbf{X}_{\lambda,n'}$.

Based on the above formulas, we can calculate the electronic structure of materials under screw symmetry within the framework of density-functional tight-binding (DFTB) theory [1, 2]. Without considering spins, the total energy E_{tot} is written as,

$$E_{\text{tot}} = \sum_{\tilde{k}} \sum_{m=1}^{n_{\text{occ}}} E_m(\tilde{k}) + \frac{1}{2} \sum_{n,n',n \neq n'} U(r_{nn'}). \quad (\text{S22})$$

The first term in Eq. (S22) is band structure energy E_{B} , which comprises electronic energies of all the occupied states. $r_{nn'}$ is the distance between atom n and n' and $U(r_{nn'})$ is the repulsive energy between these two atoms. Note that $U(r_{nn'})$ between different elements has been parametrized in DFTB method. In addition, the Hellmann-Feynman force acting on the atom n (located at \mathbf{X}_n) can be obtained,

$$\mathbf{F}_n = -\frac{\partial E_{\text{B}}}{\partial \mathbf{X}_n} = -\sum_{\tilde{k}} \sum_{m=1}^{n_{\text{occ}}} [\mathbf{C}_m^{\dagger}(\tilde{k}) \cdot \frac{\partial \mathbf{H}(\tilde{k})}{\partial \mathbf{X}_n} \cdot \mathbf{C}_m(\tilde{k}) - E_m(\tilde{k}) \mathbf{C}_m^{\dagger}(\tilde{k}) \cdot \frac{\partial \mathbf{S}(\tilde{k})}{\partial \mathbf{X}_n} \cdot \mathbf{C}_m(\tilde{k})]. \quad (\text{S23})$$

The matrix elements of derivations in Eq. (S23) are

$$\frac{\partial H_{nn',\alpha\alpha'}(\tilde{k})}{\partial \mathbf{X}_n} = \frac{1}{2N_h} \sum_{\lambda=-N_h}^{N_h-1} \exp(i\tilde{k}\lambda) \sum_{\alpha''} \frac{\partial t_{nn',\alpha\alpha''}}{\partial \mathbf{X}_n} O_{\alpha''\alpha'}(\lambda\Omega), \quad (\text{S24})$$

and

$$\frac{\partial S_{nn',\alpha\alpha'}(\tilde{k})}{\partial \mathbf{X}_n} = \frac{1}{2N_h} \sum_{\lambda=-N_h}^{N_h-1} \exp(i\tilde{k}\lambda) \sum_{\alpha''} \frac{\partial s_{nn',\alpha\alpha''}}{\partial \mathbf{X}_n} O_{\alpha''\alpha'}(\lambda\Omega). \quad (\text{S25})$$

Note that the generalized Bloch theorem [3–5] has been implemented in two packages: DFTB+ [6] and Trocadero [7], which are both based on DFTB theory [1, 2]. Having obtained total energies and Hellmann-Feynman forces, we can carry out phonon calculations which have been discussed in details in the manuscript.

S2. PHONON PROPERTIES OF TWISTED ZIGZAG GRAPHENE NANORIBBONS

The phonon properties of twisted zigzag GNRs with the width of 1.9 nm (Figs. S1-S3) and 2.8 nm (Figs. S4-S5) are shown as follows. These results show that twisting can effectively decrease phonon group velocities and indicate the reduced lattice thermal conductivity of zigzag GNRs, which are in agreement with the results of twisted armchair GNRs in the manuscript.

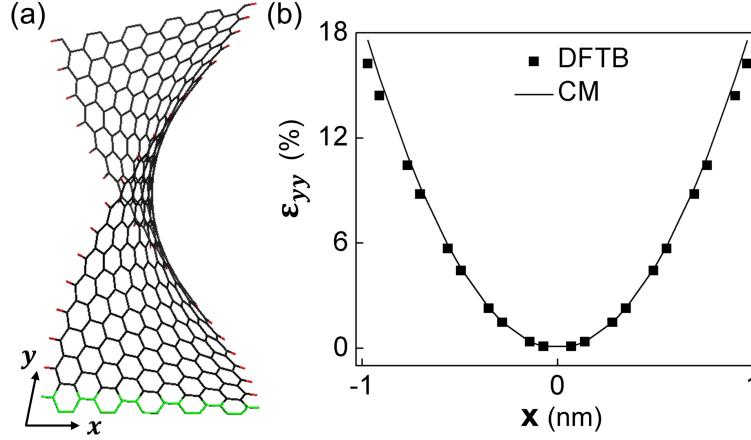


FIG. S1. (a) The relaxed structure of a 1.9-nm-wide zigzag GNR at twist rate $\gamma = 35^\circ/\text{nm}$. The edges of GNR are hydrogenated. Carbon atoms and hydrogen atoms are shown in black and red, respectively. The width is along the x direction, and the translation vector is along the y direction. Green atoms indicate the primitive motif under screw symmetry. (b) Tensile strain ϵ_{yy} versus x calculated via DFTB method based on screw symmetry and the continuum model (CM) for the twisted GNR in (a).

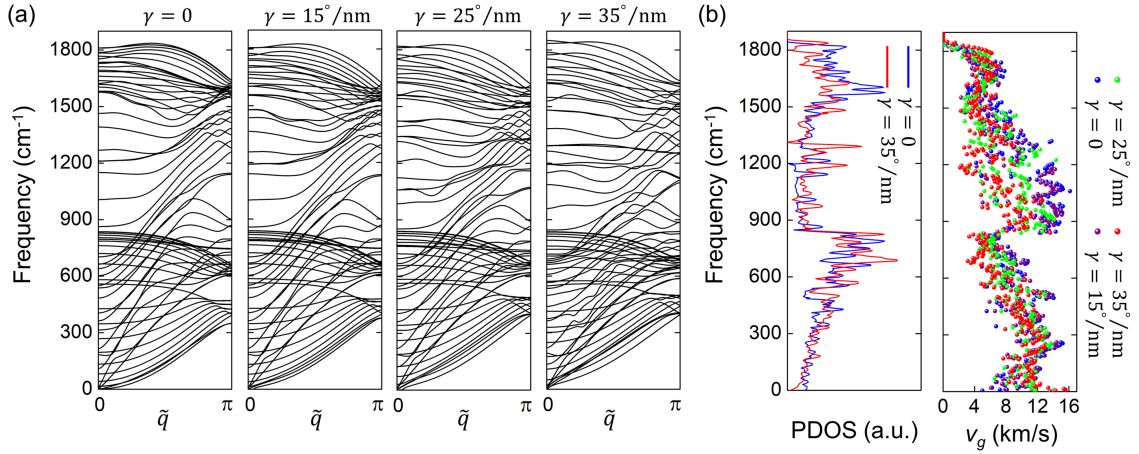


FIG. S2. (a) Phonon dispersions of 1.9-nm-wide zigzag GNRs at twist rates $\gamma = 0$, $\gamma = 15^\circ/\text{nm}$, $\gamma = 25^\circ/\text{nm}$, and $\gamma = 35^\circ/\text{nm}$ (from left to right). (b) Phonon density of state (PDOS) (left) and phonon group velocities v_g (right) calculated using the phonon dispersions in (a).

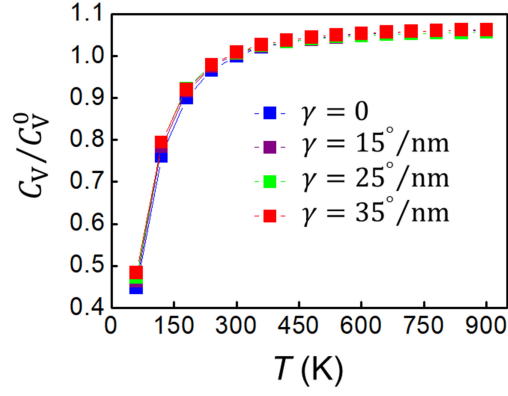


FIG. S3. Relative heat capacity C_V/C_V^0 versus temperature T for 1.9-nm-wide zigzag GNRs at twist rates $\gamma = 0$, $\gamma = 15^\circ/\text{nm}$, $\gamma = 25^\circ/\text{nm}$, and $\gamma = 35^\circ/\text{nm}$. C_V^0 denotes the heat capacity of a strain-free GNR at $T = 300$ K.

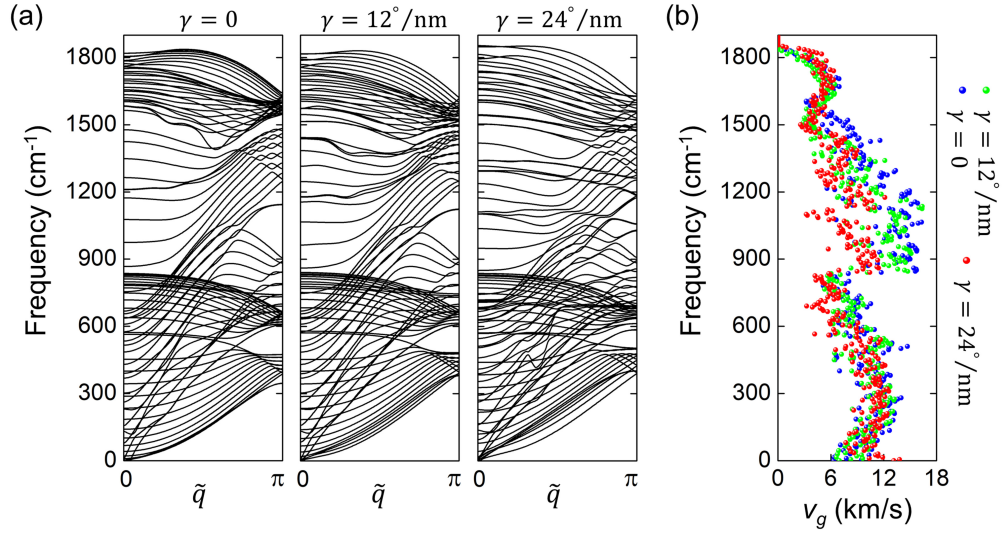


FIG. S4. (a) Phonon dispersions of 2.8-nm-wide zigzag GNRs at twist rates $\gamma = 0$, $\gamma = 12^\circ/\text{nm}$, and $\gamma = 24^\circ/\text{nm}$ (from left to right). (b) Phonon group velocities v_g calculated using the phonon dispersions in (a).

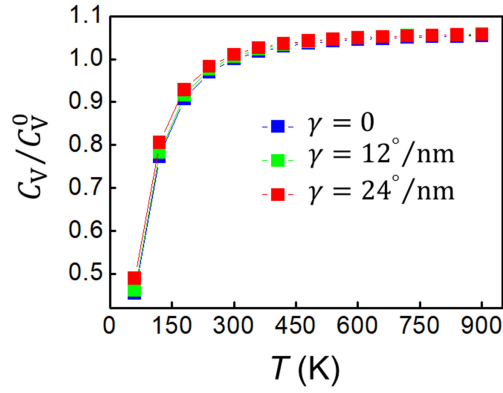


FIG. S5. Relative heat capacity C_V/C_V^0 versus temperature T for 2.8-nm-wide zigzag GNRs at twist rates $\gamma = 0$, $\gamma = 12^\circ/\text{nm}$, and $\gamma = 24^\circ/\text{nm}$. C_V^0 denotes the heat capacity of a strain-free GNR at $T = 300$ K.

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- [1] D. Porezag, Th. Frauenheim, Th. Köhler, G. Seifert, and R. Kaschner, *Phys. Rev. B* **51**, 12947 (1995).
- [2] Q. Cui, M. Elstner, E. Kaxiras, Th. Frauenheim, and M. Karplus, *J. Phys. Chem. B* **105**, 569 (2001).
- [3] X.-J. Zhao, G. Seifert, J. Zhu, and D.-B. Zhang, *Phys. Rev. B* **100**, 174202 (2019).
- [4] Z. Liu and D.-B. Zhang, *Electron. Struct.* **2**, 044001 (2020).
- [5] Z. Liu, C.-Y. Yam, S. Gao, T. Sun, and D.-B. Zhang, *New J. Phys.* **22**, 023004 (2020).
- [6] B. Hourahine, B. Aradi, V. Blum, F. Bonafé, A. Buccheri, C. Camacho, C. Cevallos, M. Y. Deshayé, T. Dumitrică, A. Dominguez, S. Ehlert, M. Elstner, T. van der Heide, J. Hermann, S. Irle, J. J. Kranz, C. Köhler, T. Kowalczyk, T. Kuba, I. S. Lee, V. Lutsker, R. J. Maurer, S. K. Min, I. Mitchell, C. Negre, T. A. Niehaus, A. M. N. Niklasson, A. J. Page, A. Pecchia, G. Penazzi, M. P. Persson, J. ezá, C. G. Sánchez, M. Sternberg, M. Stöhr, F. Stuckenberg, A. Tkatchenko, V. W.-z. Yu, and T. Frauenheim, *J. Chem. Phys.* **152**, 124101 (2020).
- [7] R. Rurali and E. Hernandez, *Comput. Mater. Sci.* **28**, 85 (2003).