significant differences. Two quantum manifestations of edge stress stand out, which are absent from the empirical prediction. One is the quantum oscillation of armchair edge stress with the increasing nanoribbon width, and the other is the reduction of zigzag edge stress by spin polarization. The physical origin of edge energy and edge stress is associated with the formation of one dangling bond on each edge atom. The repulsive interaction between the dangling bonds is believed to be one origin for the 'compressive' edge stress. In addition, in the armchair edge, it is well-known[20] that the edge dimers form triple **-C≡C-** bonds with a much shorter distance (∼ 1.23 Å according to our calculation) adding extra compressive stress to the edge; while in the zigzag edge, spin polarization further reduces the compressive stress. Therefore, quantitatively, the armchair edge has a much larger compressive stress (∼ -1.45 eV/Å) than the zigzag edge (∼ -0.5 eV/Å). In contrast, the empirical potentials predicted a smaller compressive stress in the armchair edge (∼ -1.05 eV/Å) than in the zigzag edge (∼ -2.05 eV/Å)[10].

The quantum effects in edge stress will in turn modify the mechanical edge instability. The compressive edge stress means the edge has a tendency to stretch. If we apply a uniaxial in-plane strain to a nanoribbon along the edge direction, the strain energy can be calculated as [10]

$E_{str} = 2\tau_e L\varepsilon + E_e L\varepsilon^2 + \frac{1}{2}E_s A\varepsilon^2$ (1)

Here, A is the ribbon area, L is the edge length, τ_e is the edge stress, E_e is the 1D edge elastic modulus in a 2D nanoribbon, in analogy to the 2D surface elastic modulus in a 3D nanofilm[21], and E_s is the 2D sheet elastic modulus. Since τ_e is negative, for small enough tensional strain ε (positive), the negative first term (linear to ε) in Eq. (1) can always overcome the positive second and third terms (quadratic to ε) to make E_{str} negative. Consequently, the ribbon is unstable against a small amount of stretching along the edge direction. Fitting first-principles calculations, by manually deforming the sheet and ribbon along the edge direction, to equation (1), we obtained $E_s \approx 21.09$ eV/Å^2, E_e(amchair)≈ 3 eV/Å and E_e(zigzag) ≈ 24 eV/Å with τ_e already calculated above directly (see Figs. 1 and 2). Our E_s value is in good agreement with the experiment[22] and empirical simulation result[10]. But our E_e values are notably different from the empirical results[10].

Another effective way to stretch the edge of a 2D sheet is by out-of-plane edge twisting and warping motions, which are barrierless processes. For example, assuming a sinusoidal