Nanostructural Properties
Optical & Transport Properties of Carbon Nanotubes

Assignment II
Due April 20, 2011[*]

1. You are asked to design a carbon nanotube based chemical sensor for hydrogen sulfide (H_2S), a highly toxic and noxious gas, which becomes poisonous for concentrations between 5–10 ppm, and deadly above 15 ppm. Using the data provided in Table I, calculate the change in resistance ΔR in Ω, at deadly concentrations of H_2S using the expression

$$\Delta R \approx \sum_X R_s(X)(\Theta[X, C] - \Theta[X, C_0]), \qquad (1)$$

where C is the concentration, C_0 is the concentration at standard temperature and pressure, $R_s(X) = G_0^{-1}(1/\mathrm{T}(\varepsilon_F, X) - 1/(2)$, $G_0 \equiv 2e^2/h$, $G_0^{-1} \approx 12.9$ kΩ is the quantum of conductance, and $\mathrm{T}(\varepsilon_F, X)$ is the transmission probability at the Fermi level through an active site with species X adsorbed. Note that based on the adsorption energies and concentrations given in Table I, you may argue that the coverage $\Theta[X]$ for some of the gas species listed may be neglected as being negligble. Note that for the concentration of H_2S we are considering, you may also assume $C[X] \approx C_0[X]$ for the other gases, as provided in Table I.

2. From [*Phys. Rev. B*, **73**, 205119 (2006)], for a system which is non-periodic in one dimension, but periodic in the other two (i.e. a graphene sheet, or a bulk surface), the Fourier transform of the Coulomb potential, cut -off at a distance R, is given by

$$v^{2\mathrm{D}}(\mathbf{q} + \mathbf{G}) = \frac{4\pi\left(1 + e^{-\|\mathbf{q}+\mathbf{G}_\|\|R}\left[\frac{G_z}{\|\mathbf{q}+\mathbf{G}_\|\|}\sin(G_zR) - \cos(G_zR)\right]\right)}{\|\mathbf{q} + \mathbf{G}\|^2},$$

where $\mathbf{G}_\|$ is the component of $\mathbf{G}$ in the surface/periodic direction, G_z is the component of $\mathbf{G}$ in the non-periodic direction, and $\mathbf{q}$ is the momentum transfer in the periodic direction. The Fourier transform for the Coulomb potential in real space is

$$v^{3\mathrm{D}}(\mathbf{q} + \mathbf{G}) = \frac{4\pi}{\|\mathbf{q} + \mathbf{G}\|^2}$$

For most systems $R = L/2$, where L is the length of the unit cell in the z-direction. Since $\mathbf{G}$ is the reciprocal lattice vector, so that $G_z = 2\pi n/L$, where n is an integer, give an upper bound on the cutoff correction, $\Delta = \|v^{2\mathrm{D}} - v^{3\mathrm{D}}\|/v^{3\mathrm{D}}$, for a given $\mathbf{q}$. Remember to consider the case $\mathbf{G} = 0$, although you should assume $\mathbf{q} \neq \mathbf{0}$.

3. Consider a 2D periodic system with 10 Å of vacuum between surfaces ($R = 5$ Å). How big is the cutoff correction found in Question 2 for this system if $q = 0.1$ Å^{-1}, 0.5 Å^{-1}, and 1.0 Å^{-1}.

4. Suppose a converged DFT calculation has been performed with 10 Å of vacuum $d_{\mathrm{vacuum}} = 10$ Å, but with a 20 Å thick bulk slab $d_{\mathrm{slab}} = 20$ Å, giving a total unit cell length of L =30 Å in the non-periodic direction. How much, if any, zero-padding (i.e. empty unit cells of vacuum) must we introduce into the calculation before it is valid to employ a cutoff in the Coulomb potential? In other words, how many unit cells of vacuum must be added to obtain a radial cutoff R which is less than half the vacuum separation, and still greater than the bulk slab thickness, so that $d_{\mathrm{slab}} \lesssim R \lesssim d_{\mathrm{vacuum}}/2$. Please justify.

5. Provide an upper bound for the cutoff correction in Question 4. How much zero-padding must be instead employed before the cutoff correction is less than 1%?

TABLE I: Equilibrium atmospheric concentrations $C[X]$, gas phase entropies $S_{\mathrm{gas}}[X]$, transmission, and adsorption energies $E_{\mathrm{ads}}[X]$, on a TM@CNT, at $T = 300$ K.

X	$C[X]$	$E_{\mathrm{ads}}[X]$	$S_{\mathrm{gas}}[X]$	$\mathrm{T}(\varepsilon_F, X)$
N_2	74.96%	-0.65 eV	1.988 meV/K	1.332
O_2	20.11%	-2.13 eV	2.128 meV/K	1.492
H_2O	4.00%	-0.79 eV	1.959 meV/K	1.427
CO	96.00 ppb	-1.14 eV	2.050 meV/K	0.608
NH_3	16.32 ppb	-1.07 eV	2.000 meV/K	1.498
H_2S	0.96 ppb	-2.74 eV	2.136 meV/K	1.427

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