MSE 102, Fall 2017 Midterm #2

Write your name here: Solutions

Instructions:

- Answer all questions to the best of your abilities. Be sure to write legibly and state your answers clearly.
- The point values for each question are indicated.
- You are not allowed to use notes, friends, phones, etc. You may use a calculator.
- You should circle your answer.
- There are a total of 100 points.
- Feel free to ask questions, but only for clarification purposes.

problem	
1	/20
2	/20
3	/25
4	/25
total	/100

1. When noble gases condense on a surface, they can be considered to form a 2-D crystal. Suppose that the 2D crystal can be described quite well using the potential:

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{14} - \left(\frac{\sigma}{r}\right)^{6}\right].$$

Note that the repulsive term is given by the 14th power of $\left(\frac{\sigma}{r}\right)$, not the 12th power associated with the Lennard-Jones potential.

(a) **[20 points]** *Derive* the equilibrium lattice parameter, and the energy per atom of a one atom per unit cell 2D crystal defined on a simple hexagonal lattice with primitive lattice vectors:

$$\mathbf{a} = -\frac{1}{2}a_o\,\mathbf{e}_1 - \frac{\sqrt{3}}{2}a_o\,\mathbf{e}_2$$
$$\mathbf{b} = a_o\,\mathbf{e}_1$$

.

You should express your answers algebraically in terms of the constants σ, ε, and the relevant dimensionless sums given below. (You don't need to substitute the numbers… they are given merely for reference.)

$$A_{14} = \sum_{u,v=-\infty}^{\infty} \frac{1}{(u^2 - u\,v + v^2)^7} = 2.00288,$$

$$A_6 = \sum_{u,v=-\infty}^{\infty} \frac{1}{(u^2 - u\,v + v^2)^3} = 2.30651.$$

We have that $\underset{\sim}{R}_{uv} = u\underset{\sim}{a} + v\underset{\sim}{b}$

$$= \left(v - \frac{u}{2}\right)a_o\,\underset{\sim}{e}_1 - u\frac{\sqrt{3}}{2}\,\underset{\sim}{e}_2$$

$\therefore$

$$\underset{\sim}{R}_{uv} \cdot \underset{\sim}{R}_{uv} = a_o^2\left(v - \frac{u}{2}\right)^2 + \frac{3}{4}u^2 a_o^2$$

$$= \left(v^2 - uv + \frac{u^2}{4} + \frac{3}{4}u^2\right)a_o^2$$

$$= \left(u^2 - uv + v^2\right)a_o^2$$

$$e = \frac{E}{N_L} = 2\varepsilon \sum_{uv}{}' \left\{ \left(\frac{\sigma}{a_0}\right)^{14} \frac{1}{(u^2-uv+v^2)^7} - \left(\frac{\sigma}{a_0}\right)^{6} \frac{1}{(u^2-uv+v^2)^3} \right\}$$

$$= 2\varepsilon \left\{ A_{14}\left(\frac{\sigma}{a_0}\right)^{14} - A_6\left(\frac{\sigma}{a_0}\right)^{6} \right\}$$

$$\frac{de}{da_0} = 0 = \frac{-14}{a_0} A_{14}\left(\frac{\sigma}{a_0}\right)^{14} + \frac{6A_6}{a_0}\left(\frac{\sigma}{a_0}\right)^{6}$$

$$\Rightarrow \quad 14\, A_{14}\left(\frac{\sigma}{a_0}\right)^{8} = 6A_6$$

or $$\left(\frac{7}{3}\frac{A_{14}}{A_6}\right)^{1/8} \sigma = a_0.$$

Substituting, into the expression for the energy we have:

$$e = 2\varepsilon \left\{ A_{14} \frac{1}{\left(\frac{7}{3}\frac{A_{14}}{A_6}\right)^{14/8}} - A_6 \frac{1}{\left(\frac{7}{3}\frac{A_{14}}{A_6}\right)^{6/8}} \right\}$$

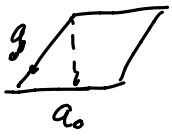
$$= 2 \frac{A_6^{7/4}}{A_{14}^{3/4}} \left\{ \left(\frac{3}{7}\right)^{14/8} - \left(\frac{3}{7}\right)^{6/8} \right\} \varepsilon$$

$$= -2 \frac{A_6^{7/4}}{A_{14}^{3/4}} \left(\frac{3}{7}\right)^{6/8} \frac{4}{7}\varepsilon = -\frac{8}{7} \frac{A_6^{7/4}}{A_{14}^{3/4}} \left(\frac{3}{7}\right)^{3/4} \varepsilon$$

(b) **[10 points]** We can define an elastic modulus of a 2D material equivalent to the bulk modulus of a 3D material, B, using the relationship:

$$B = A_o \left.\frac{d^2 e}{dA^2}\right|_{A=A_o} ,$$

where A_o is defined to be the area per atom at equilibrium, A is the actual area per atom, and e is the energy per atom. Compute a value of B in terms of the constants σ, ε, and the dimensionless sums given above, and the equilibrium lattice parameter.

To solve this problem we need to convert the expression for the energy/site to depend on area. We note that the area of the unit cell is  $= \frac{\sqrt{3}}{2} a_o^2$. $\therefore A_o = \frac{\sqrt{3}}{2} a_o^2$

$A = \frac{\sqrt{3}}{2} a^2$. We can write e in terms of a:

$$e = 2\varepsilon \left\{ A_{14} \left(\frac{\sigma}{a}\right)^{14} - A_6 \left(\frac{\sigma}{a}\right)^6 \right\}$$

$$= 2\varepsilon \left\{ A_{14} \frac{\sigma^{14}}{(a^2)^7} - A_6 \frac{\sigma^6}{(a^2)^3} \right\}$$

$$= 2\varepsilon \left\{ A_{14} \frac{\sigma^{14}}{(2A/\sqrt{3})^7} - A_6 \frac{\sigma^6}{\left(\frac{2A}{\sqrt{3}}\right)^3} \right\}$$

$$= 2\varepsilon \left\{ A_{14} \frac{3^{7/2}}{2^7} \frac{\sigma^{14}}{A^7} - A_6 \frac{3^{3/2}}{2^3} \frac{\sigma^6}{A^3} \right\}$$

$$\frac{\partial e}{\partial A} = 2\varepsilon \left\{ -7 A_{14} \frac{3^{7/2}}{2^7} \frac{\sigma^{14}}{A^8} + 3 A_6 \frac{3^{3/2}}{2^3} \frac{\sigma^6}{A^4} \right\}$$

$$\frac{\partial^2 e}{\partial A^2} = 2\varepsilon \left\{ +56 A_{14} \frac{3^{7/2}}{2^7} \frac{\sigma^{14}}{A^9} - 12 A_6 \frac{3^{3/2}}{2^3} \frac{\sigma^6}{A^5} \right\}$$

$\therefore$

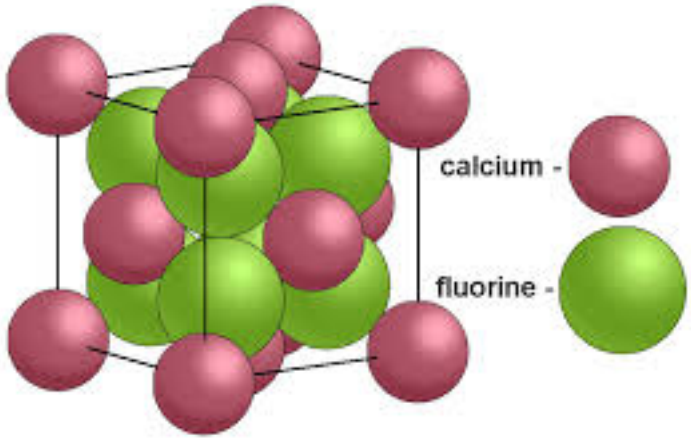
$$B = 2\varepsilon \left\{ 56 A_{14} \frac{3^{7/2}}{2^7} \frac{\sigma^{14}}{A_0^8} - 12 A_6 \frac{3^{3/2}}{2^3} \frac{\sigma^6}{A_0^4} \right\}$$

$$A_0^8 = \left(\frac{3}{4}\right)^4 a_0^{16} \qquad A_0^4 = \left(\frac{3}{4}\right)^2 a_0^8$$

$$B = 2\varepsilon \left\{ 56 A_{14} \frac{3^{7/2}}{2^7} \frac{\sigma^{14}}{\left(\frac{3}{4}\right)^4 a_0^{16}} - 12 A_6 \frac{3^{3/2}}{2^3} \frac{\sigma^6}{\left(\frac{3}{4}\right)^2 a_0^8} \right\}$$

$$B = 2\varepsilon \left\{ 56 \frac{2}{\sqrt{3}} A_{14} \left(\frac{\sigma^{14}}{a_0^{14}}\right) - 12 A_6 \frac{2}{\sqrt{3}} \left(\frac{\sigma^4}{a_0^8}\right) \right\}$$

with $a_0 = \left(\frac{7}{3} \frac{A_{14}}{A_6}\right)^{1/8} \sigma$.



2. **[20 points]** CaF_2 is a compound that forms ionically with the structure shown above. The Ca atoms are positioned on the sites of a cubic F-lattice. Each Ca atom is surrounded by 8 F atoms, positioned at the tetrahedral interstitial sites. The experimentally measured formation enthalpy (per formula unit) is:

$$\Delta H = -12.7\ eV.$$

The sublimation energy of Ca is $S_{Ca} = 1.84\ eV$, and the dissociation energy of F is $D_F = 1.65\ eV$. In addition, we have

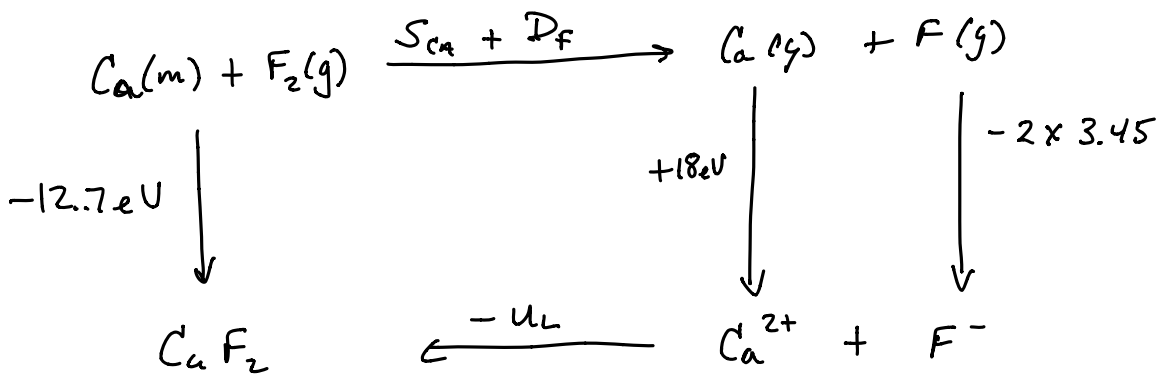
$$Ca + 18.0\ eV \rightarrow Ca^{2+} + 2\ e^-$$

and

$$F^- + 3.45\ eV \rightarrow F + e^-.$$

Use the Born-Haber cycle to estimate the experimental value of the lattice formation energy (i.e. the reduction in energy per formula unit associated with assembling the ions into the CaF_2 structure, assuming the ions start out separated by infinite distances).

The Born Haber cycle looks like this:



We have

$$-12.7\ eV = 1.84\ eV + 1.65\ eV + 18.0\ eV - 6.90\ eV - U_L$$

$$-U_L = -12.7 - 18.0 - 1.84 - 1.65 + 6.90$$

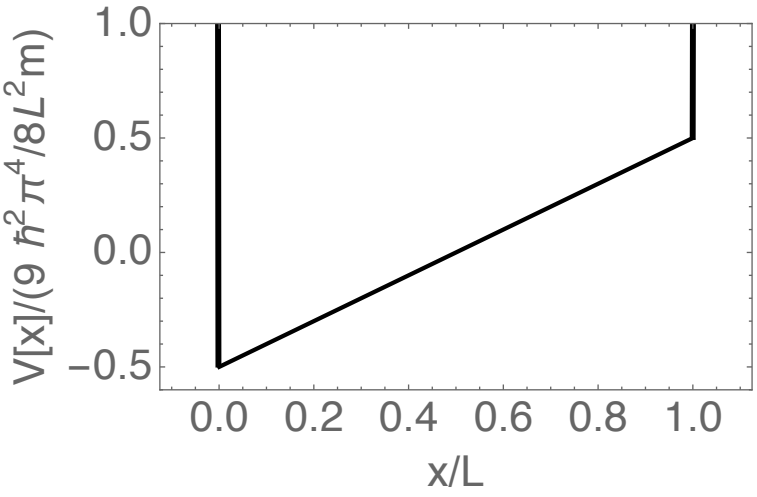
$$= -27.3\ eV$$

So energy is reduced by 27.3 eV upon forming crystal.

3. **[25 points]** A finite length wire is prepared with a single electron. The potential of the wire is then tuned to have the following properties:

$$V(x) = \begin{cases} \infty & x < 0 \\ 9\frac{\hbar^2\pi^4(x-\frac{L}{2})}{8L^3\mathrm{m}} & 0 \le x \le L \\ \infty & x > L \end{cases}.$$

Here, *m* is the mass of the electron. The potential, when plotted, looks like.



Compute an estimate for the ground state energy of the electron. To do this, you will use the orthonormal functions $\psi_1(x)$ and $\psi_2(x)$ as a basis, where:

$$\psi_n(x) = \sqrt{\frac{2}{L}} sin\left(\frac{n\,\pi}{L}x\right).$$

You will need the integral:

$$\int_0^L dx\ \psi_n(x)V(x)\psi_p(x) = \begin{cases} 9\frac{\pi^2\hbar^2}{2L^2\mathrm{m}}\frac{(-1+(-1)^{n+p})np}{(n^2-p^2)^2} & n \neq p \\ 0 & n = p \end{cases}.$$

Using this basis, construct the Hamiltonian matrix and find its lowest eigenvalue. (Don't forget to include the kinetic energy – I've only given you the matrix element of the potential energy term.) Express your answer in terms of $\frac{\pi^2\hbar^2}{2L^2\mathrm{m}}$.

$$H = \begin{pmatrix} \int \psi_1^* \hat{H} \psi_1 \, dx & \cdots \\ & \end{pmatrix}$$

$$H_{11} = +\frac{\hbar^2}{2m}\frac{\pi^2}{L^2} \qquad H_{12} = \frac{9\pi^2\hbar^2}{2L^2m}\frac{(-1-1)\,2}{9}$$

$$H_{22} = +\frac{\hbar^2}{2m}\frac{4\pi^2}{L^2} \qquad = -4\frac{\pi^2\hbar^2}{2L^2m}$$

$$\underline{\underline{H}} = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}\begin{pmatrix} 1 & -4 \\ -4 & 4 \end{pmatrix}$$

The eigenvalues are given by

$$(1-E)(4-E) - 16 = 0$$

$$E^2 - 5E - 12 = 0$$

$$E = \frac{5 \pm \sqrt{25+48}}{2} = \frac{5}{2} \pm \frac{\sqrt{73}}{2}$$

$\therefore$ lowest energy $= \left(\frac{5}{2} - \frac{\sqrt{73}}{2}\right)\frac{\hbar^2}{2m}\frac{\pi^2}{L^2}$

4. A hydrogen atom is prepared in the state:

$$\Psi(x, t = 0) = \frac{1}{\sqrt{2}}\psi_{100}(\boldsymbol{r}) - \frac{i}{\sqrt{2}}\psi_{21-1}(\boldsymbol{r}).$$

[5 points] Give an expression for the wavefunction at times $t > 0$.

$$\Psi(x,t) = \frac{1}{\sqrt{2}} e^{-iE_1 t/\hbar} \psi_{100}(\underline{r}) - \frac{i}{\sqrt{2}} e^{-iE_2 t/\hbar} \psi_{21-1}(\underline{r})$$

with $E_n = \frac{-R}{n^2}$, $R = -13.6\ eV$

[5 points] What is the expectation value of the total energy?

$$\frac{E_1 + E_2}{2} = -\frac{R}{2}\left(\frac{1}{1} + \frac{1}{4}\right) = \frac{-5}{8} R$$

[5 points] What is the expectation value of the square of the angular moment?

$$\frac{1}{2}\hbar^2(1)(1+1) = \hbar^2$$

[5 points] What is the expectation value of the z-component of the angular momentum?

$$-\frac{1}{2}\hbar$$

[5 points] Suppose that at time $t = t_o$ you measure the energy to be E_2. What value will a subsequent measurement of the energy yield (provided no other quantities have been measured in between the time t_o and the second measurement)?

E_2