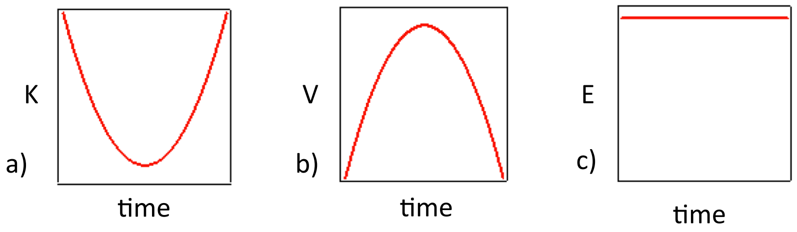
Understanding Physical Chemistry

Solutions to Homework Problems in Chapter 1

September 11, 2013

1.



The total energy, E is the sum of kinetic, K and potential, V energies. Unless the ball is thrown straight up, there is some minimum value of K>0, because the baseball will still be moving at the top of its trajectory, which is also where V reaches its maximum value. The total energy is conserved if there is no friction, and equivalent to the initial value of K (because we may assume that the baseball has zero potential energy when it is at ground level). In the absence of friction, the final kinetic energy is exactly equal to its initial value, and the total energy is constant. The situation is expected to be quite different when the effects of friction are included, as described below.

d)When a baseball is hit into the air it experiences wind resistance, which slows it down and gradually drains its total energy. As a result, the ball will not travel as far, or fly as high, as it would have if there were no wind resistance. The total energy of the baseball is the sum of its kinetic and potential energies. The kinetic energy of the ball is proportional to the square of its velocity. The rate at which the energy of the ball is drained by wind resistance is also expected to be proportional to the square of its velocity. So, the ball will experience the most wind resistance when it's kinetic energy is largest. The potential energy of the ball depends on its elevation, and so it will have the same potential energy when it is caught as it did when it was hit. Since wind resistance drains the total energy of the baseball, its final velocity must be smaller than it was when it was hit. The difference between the final and initial kinetic energy of the baseball is exactly equal to the amount of energy which the ball lost due to wind resistance.

2. $K = \frac{1}{2}mv^2$ Note that the SI unit of energy is a Joule, $\mathrm{J} = \mathrm{N} \times \mathrm{m} = \mathrm{kg} \times \mathrm{m}^2/\mathrm{s}^2$

a)

$$m = 5.25\mathrm{oz} \times \frac{28.35\mathrm{g}}{\mathrm{oz}} \times \frac{\mathrm{kg}}{1000\mathrm{g}} = 0.1488\mathrm{kg}$$

$$v = 20\text{mph} \times \frac{1.609\text{km}}{\text{mi}} \times \frac{1000\text{m}}{\text{km}} \times \frac{\text{h}}{3600\text{s}} = 8.939\text{m/s}$$

$$K = \frac{1}{2} \times 0.1488\text{kg} \times (8.939\text{m/s})^2 = 6.0\text{J}$$

b)

$$m = 175\text{lb} \times \frac{0.4536\text{kg}}{\text{lb}} = 79.38\text{kg}$$

$$K = \frac{1}{2} \times 79.38\text{kg} \times (8.939\text{m/s})^2 = 3171\text{J} = 3.17\text{kJ}$$

c)

$$\frac{K^{ball}}{K^{bike}} = \frac{\frac{1}{2}m^{bike}(v^{bike})^2}{\frac{1}{2}m^{ball}(v^{ball})^2} = 1$$

$$\frac{v^{ball}}{v^{bike}} = \left(\frac{m^{bike}}{m^{ball}}\right)^{1/2} = \left(\frac{79.38}{0.1488}\right)^{1/2} = 23$$

3.

a) The force along the slope is $F_z = -mg\sin\theta$ (as explained in Exercise 1.1 on pages 7-8). To obtain the force in SI units (m, kg, s) we need to use $m = 2000$ kg, $g = 9.8$ m/s^2, and $\sin\theta = \sin(-26.6°) =$ -0.448, so the force is $F_z \sim 8780$ kg/(m s^2) = 8780 N. If we had defined the angle as positive, then the sign of the force would have become negative. In other words, we have chosen signs that are consistent with this downhill force being a positive number.

b) Assuming no energy is lost to friction, energy is conserved such that the final kinetic energy is equal to the potential energy at the top of the hill ($K = V_0$).

$$V_0 = mgh = 2000\text{kg} \times 9.8\text{m/s}^2 \times 30\text{m} = 588\text{kJ} \approx 590\text{kJ}$$

c) The maximum speed of the car will occur at the bottom of the hill.

$$K = \frac{1}{2}mv^2 \Rightarrow v = \left(\frac{2K}{m}\right)^{1/2} = \left(\frac{2 \times 588 \times 10^3\text{J}}{2000\text{kg}}\right)^{1/2} = 24.25\text{m/s}$$

$$24.25\frac{\text{m}}{\text{s}} \times \frac{1\text{mi}}{1609\text{m}} \times \frac{3600\text{s}}{\text{h}} = 54\text{mph}$$

4.
a) $e^- + p^+ = 2\gamma$ The total mass of the particles is converted to energy. The total energy of the product is,

$$E = mc^2 = (m_e + m_p)c^2 = 2m_ec^2 = 2 \times 9.109 \times 10^{-31}\text{kg} \times (3.0 \times 10^8\text{m/s})^2 = 1.64 \times 10^{-13}\text{J}$$

The energy per gamma photon is $\frac{1}{2}(1.64 \times 10^{-13}\text{J}) = 8.2 \times 10^{-14}\text{J}$.

b) The energy per mole of photons is

$$8.2 \times 10^{-14}\frac{\text{J}}{\gamma} \times \frac{6.02 \times 10^{23}\gamma}{\text{mol}} \times \frac{\text{kJ}}{1000\text{J}} = 4.9 \times 10^7\text{kJ/mol}$$

c) And in eV per gamma photon...

$$8.2 \times 10^{-14}\text{J} \times \frac{1\text{eV}}{1.602 \times 10^{-19}\text{J}} = 5.1 \times 10^5\text{eV} = 0.51\text{MeV}$$

5.
a)

$$F = -\left(\frac{dV}{dx}\right) = ma$$

b)

$$\frac{dv}{dt} = a$$

$$\int_0^v dv = \int_0^t a\ dt$$

$$v = at$$

c)

$$\frac{dx}{dt} = v$$

$$\int_0^x dx = \int_0^t v\ dt = \int_0^t at\ dt$$

$$x = \frac{1}{2}at^2$$

d) Both mass and acceleration are constant and so the force is constant. The total work done on the object should be equal to its final kinetic energy, which can be demonstrated as follows (and making use of the fact that $v = at$, as shown above):

$$W = F\int_0^x dx = ma\left(\frac{a}{2}t^2\right) = \frac{1}{2}m(at)^2 = \frac{1}{2}mv^2 = K.$$

6. The photoelectric formula is $KE = h\nu - \Phi$, which can be modeled by the linear equation $y(x) = mx + b$. Plotting the kinetic energy, KE, as a function of the frequency, ν, will yield a line with a slope of Planck's constant, $dy/dx = h$.

7. The binding energy Φ of the electron is equivalent to the difference between the photon energy and the kinetic energy of the ejected electron $\Phi = h\nu - KE$. Converting wavelength to frequency,

$$\nu = \frac{3.00 \times 10^8 \text{m/s}}{253.5\text{nm} \times 1\text{m}/10^9\text{nm}} \approx 1.18 \times 10^{15}\text{Hz}$$

Solving for Φ,

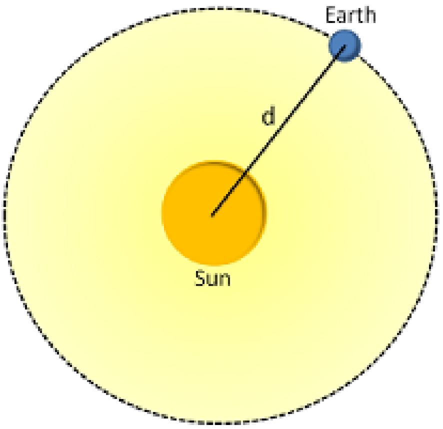
$$\Phi = (6.6 \times 10^{-34}\text{J} \cdot \text{s}) \times \left(\frac{1\text{eV}}{1.6 \times 10^{-19}\text{J}}\right) \times (1.18 \times 10^{15}\text{s}^{-1}) - 0.8\text{eV}$$

$$\Phi = 4.09\text{eV} \approx 4\text{eV}.$$

8. a) The amount of energy hitting the earth per second

$$1400\frac{\text{J/s}}{\text{m}^2} \times 1\text{m}^2 \times 1\text{s} = 1400\text{J}$$

which is the rate work could theoretically be obtained from sunlight shining on a square meter.



b) To calculate the number of photons striking 1 square meter of the earth in one second, we calculate the individual energy contribution from each photon then divide into the total energy:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\text{J} \cdot \text{s})(3 \times 10^8\text{m/s})}{5 \times 10^{-7}\text{m}} = 3.98 \times 10^{-19}\text{J/photon}$$

$$1400\text{J} \times \frac{1\text{photon}}{3.98 \times 10^{-19}\text{J}} = 3.52 \times 10^{21}\text{photons}$$

c)If we know the power output at a certain distance from the sun and assume uniform distribution, then the total power is obtained by calculating the power radiating in all directions. This is achieved by calculating the output in terms of the surface area of a shell encompassing the sun.

$$1400\frac{\text{W}}{\text{m}^2} \times 4\pi(150 \times 10^9\text{m})^2 = 3.96 \times 10^{26}\text{W}$$

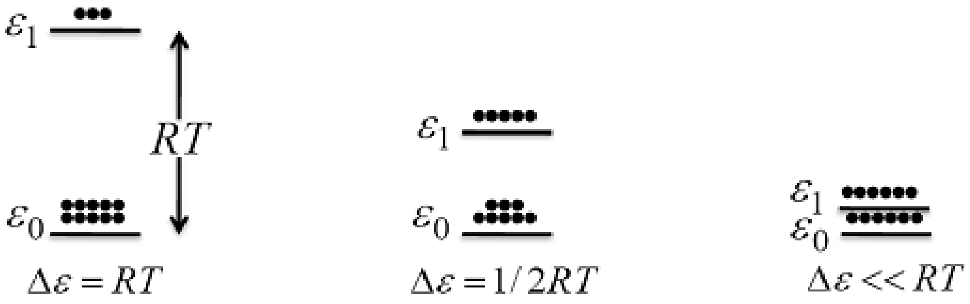
9. a) The ratio of excited to ground state population is

$$\frac{P(\epsilon_1)}{P(\epsilon_0)} = \frac{e^{-\beta\epsilon_1}/q}{e^{-\beta\epsilon_0}/q} = e^{\frac{-\Delta\epsilon}{RT}} = e^{\frac{-2.5\text{kJ/mol}}{2.5\text{kJ/mol}}} = e^{-1} = 0.37$$

b) Increasing the temperature by a factor of 2 gives $R(2T) = 5$ kJ/mol

$$\frac{P(\epsilon_1)}{P(\epsilon_0)} = e^{\frac{-2.5\text{kJ/mol}}{5\text{kJ/mol}}} = e^{-1/2} = 0.61$$

This result makes sense since at higher temperature there is a greater probability of finding the system in its excited state. At very high temperature, when RT approaches infinite, $\lim_{RT\to\infty} e^{-\frac{\Delta\epsilon}{RT}} = 1$, the population is expected to become equally distributed in both states. In other words, when RT is much larger than the energy level spacing $\Delta\epsilon$, the difference between two states becomes indistinguishable on the scale of RT.



c) The resonant frequency $\tilde{\nu} = 565\text{cm}^{-1}$ can be converted to the energy difference $\Delta\epsilon$ between the ground and excited state using $\Delta\epsilon = hc\tilde{\nu}$.

$$\frac{P(\epsilon_1)}{P(\epsilon_0)} = e^{\frac{hc\tilde{\nu}}{k_BT}} = e^{-\frac{565\text{cm}^{-1}}{209\text{cm}^{-1}}} = 0.067$$

Note that $\frac{hc}{k_BT} = 1/209\text{cm}^{-1}$ was given in the problem.

d) Introducing degeneracy into the probability equations incorporates contributions from multiple states with the same energy.

$$\frac{P(\epsilon_1)}{P(\epsilon_0)} = \frac{g_1}{g_0}e^{\frac{hc\tilde{\nu}}{k_BT}} = 3e^{-\frac{0.5\text{cm}^{-1}}{209\text{cm}^{-1}}} = 2.99 \approx 3$$

Since $k_B T$ (or RT) is large with respect to the energy spacing, the ratio of the excited and ground state probabilities is now dictated by the ratio of the corresponding degeneracies.

10. a) Following the description the sub-section entitled Chemical Reaction Equilibrium Constant on pages 25-26,

$$K = \frac{[u]}{[f]} = \frac{P(u)}{P(f)} = \frac{g_u}{g_f} e^{-\frac{\epsilon_u - \epsilon_f}{RT}}$$

b) If the degeneracy ratio is 1, then taking the natural log of the following equations yields the energy difference, $\Delta\epsilon = \epsilon_u - \epsilon_f$

$$K = e^{-\frac{\Delta\epsilon}{RT}}$$

$$\ln K = -\frac{\Delta\epsilon}{RT}$$

$$\Delta\epsilon = -RT \ln K = -8.314 \frac{\mathrm{J}}{\mathrm{K \cdot mol}} \times 293.14\mathrm{K} \times \ln 0.4 = 2.2\mathrm{kJ/mol}$$

c) Solving for the degeneracy ratio given $\Delta\epsilon = 20\mathrm{kJ/mol}$,

$$\frac{g_u}{g_f} = K e^{\frac{\Delta\epsilon}{RT}} = 0.4 e^{\frac{20{,}000\mathrm{J/mol}}{8.314\mathrm{J/K \cdot mol} \times 293.15\mathrm{K}}} = 1465$$

There are about 1500 unfolded conformations. This makes sense since there are many unfolded conformations but only one which is folded. It is also interesting to note that, since $RT = 2.5$ kJ/mol at room temperature, this analysis suggests that there are approximately $(g_u/g_f)e^{-\Delta\varepsilon/RT} \sim 1200$ unfolded proteins for every one folded protein, at room temperature.

11. The partition function is $q = \sum_i g_i e^{-\beta\varepsilon_i} = g_0 e^{-\beta\varepsilon_0} + g_1 e^{-\beta\varepsilon_1} = g_0 + g_1 e^{-\beta\Delta\varepsilon}$.

a) At very low temperature $\beta \to \infty$, $\beta\Delta\varepsilon \to \infty$, and $e^{-\beta\Delta\varepsilon} \to 0$ so $q = g_0$. That makes sense, since at low temperature only the ground state should be populated, and so the total number of thermally populated states should be the same as the degeneracy of the ground state.

b) At very high temperature $\beta \to 0$, $\beta\Delta\varepsilon \to 0$, and $e^{-\beta\Delta\varepsilon} \to 1$, so $q = g_0 + g_1$. This also makes sense, since at very high temperature all of the states should be equally populated, so the total number of populated states should be the sum of the degeneracies of the all the energy levels.

c) From Eq. 1.23 for the average energy at *any* temperature.

$$\langle\varepsilon\rangle = -\frac{1}{q}\left(\frac{d\, q}{d\beta}\right) = \frac{g_1 \Delta\varepsilon e^{-\beta\Delta\varepsilon}}{g_0 + g_1 e^{-\beta\Delta\varepsilon}} = \frac{g_1 \Delta\varepsilon}{g_0 e^{+\beta\Delta\varepsilon} + g_1}$$

For example, note that this is consistent with our expectation that $\langle\varepsilon\rangle = 0$ at very low temperature, while at very high temperature the above expression becomes $\langle\varepsilon\rangle = \Delta\varepsilon[g_1/(g_0 + g_1)]$, which is also physically reasonable. Note that if $g_0 = g_1 = 1$ then we would expect that at very high temperature $\langle\varepsilon\rangle = \frac{1}{2}\Delta\varepsilon$, which is consistent with the above result.

12. a) The vibrational contribution to the heat capacity at constant volume is equal to the slope of the average vibrational energy, $\langle\epsilon\rangle$, with respect to temperature, T.

$$C_V^{vib} = \frac{d\langle\epsilon\rangle}{dT}$$

Alternatively, we can express the heat capacity as a derivative with respect to β using the chain rule:

$$\frac{d\langle\epsilon\rangle}{dT} = \frac{d\langle\epsilon\rangle}{d\beta}\frac{d\beta}{dT}$$

$$\frac{d\beta}{dT} = -\frac{1}{RT^2}$$

$$C_V^{vib} = -\frac{1}{RT^2}\frac{d\langle\epsilon\rangle}{d\beta}$$

Differentiating $\langle\epsilon\rangle$ from Equation 1.24 with respect to β yields

$$\frac{d\langle\epsilon\rangle}{d\beta} = \frac{d}{d\beta}\frac{\Delta\epsilon}{e^{\beta\Delta\epsilon}-1} = -\frac{\Delta\epsilon}{(e^{\beta\Delta\epsilon}-1)^2}\frac{d}{d\beta}e^{\beta\Delta\epsilon} = -\frac{(\Delta\epsilon)^2 e^{\beta\Delta\epsilon}}{(e^{\beta\Delta\epsilon}-1)^2}$$

Multiplying by $-(RT^2)^{-1}$ will give Equation 1.25, after the following additional manipulations

$$C_V^{vib} = -\frac{1}{RT^2}\left(-\frac{(\Delta\epsilon)^2 e^{\beta\Delta\epsilon}}{(e^{\beta\Delta\epsilon}-1)^2}\right) = \left(\frac{R}{R}\right)\frac{1}{RT^2}\left(\frac{(\Delta\epsilon)^2 e^{\beta\Delta\epsilon}}{(e^{\beta\Delta\epsilon}-1)^2}\right) = R\frac{(\beta\Delta\epsilon)^2 e^{\beta\Delta\epsilon}}{(e^{\beta\Delta\epsilon}-1)^2}$$

b) Equation 1.26 can be used to predict the molar heat capacity of Cl_2 at 300 K:

$$\frac{C_V}{R} = \frac{5}{2} + \frac{(\beta\Delta\epsilon)^2 e^{\beta\Delta\epsilon}}{(e^{\beta\Delta\epsilon}-1)^2}$$

From problem 9c, we know $\beta\Delta\epsilon = 2.7$ and so the above expression yields the following result

$$\frac{C_V}{R} = \frac{5}{2} + \frac{(2.7)^2 14.87}{(14.87-1)^2}$$

$$C_V = 3.06\left(8.314\frac{\mathrm{J}}{\mathrm{K\cdot mol}}\right) = 25.47\left(\frac{\mathrm{J}}{\mathrm{K\cdot mol}}\right)$$

This is very close to the experimental value of 26 $\frac{\mathrm{J}}{\mathrm{K\cdot mol}}$.

13. a) The Hamiltonian is the sum of the kinetic and potential energies, $H = K + V$. A particle confined to one dimension has one translational degree of freedom which is a quadratic function of v, and and additional quadratic term that arises from the harmonc potential energy, so the total vibrational Hamiltonian is

$$H = \frac{1}{2}mv^2 + Ax^2$$

b) Since the kinetic energy gives rise to a single quadratic term in the Hamiltonian, the average kinetic energy is

$$\langle K\rangle = \frac{1}{2}k_BT.$$

c) The Virial Theorem relates the ratio to the kinetic and potential energies for any system whose potential energy has the following form $V(r) = ar^n$. For a harmonic potential n = 2, thus

$$\frac{\langle V \rangle}{\langle K \rangle} = \frac{2}{n} = \frac{2}{2} = 1.$$

Using the information from part b, we can solve for the average potential energy to get

$$\langle V \rangle = \langle K \rangle = \frac{1}{2} k_B T.$$

exactly as expected, given that each quadratic term in the Hamiltonian is predicted to have an average thermal energy of $\frac{1}{2} k_B T$ (when it behaves classically).

d) The functional form of the kinetic energy is again a quadratic function of velocity $K = \frac{1}{2} m v^2$ and so the average kinetic energy is once again $\langle K \rangle = \frac{1}{2} k_B T$. We may now use the Virial Theorem (as in c) to determine the average potential energy of this system, for which n = 6,

$$\frac{\langle V \rangle}{\langle K \rangle} = \frac{2}{6}$$

$$\langle V \rangle = \frac{1}{3} \langle K \rangle = \frac{1}{3} \times \frac{1}{2} k_B T$$

$$\langle V \rangle = \frac{1}{6} k_B T.$$

14. a) From Equation 1.33

$$P(v)dv = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} 4\pi v^2 dv$$

The average speed is

$$\langle v \rangle = \int_0^\infty v P(v) dv = b \int_0^\infty v^3 e^{-av^2} dv$$

where we define $b = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2}$ and $a = \frac{m}{2k_B T}$.

The general solution to an integral of this form is (see Appendix B)

$$\int_0^\infty x^m e^{-ax^2} = \frac{\Gamma[(m+1)/2]}{2a^{(m+1)/2}}$$

For m=3,

$$\frac{\Gamma[2]}{2a^2} = \frac{1!}{2a^2} = \frac{1}{2a^2}$$

Remembering that $a = \frac{m}{2k_B T}$, the solution is

$$\langle v \rangle = \frac{b}{2a^2} = \frac{4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2}}{2 \left(\frac{m}{2k_B T} \right)^2} = \frac{2\pi m^{3/2} (2k_B T)^2}{m^2 (2\pi k_B T)^{3/2}} = 2\sqrt{\frac{2k_B T}{\pi m}} = \sqrt{4}\sqrt{\frac{2k_B T}{\pi m}}$$

$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

The last step was performed recalling $m = M/N_A$ and $k_B = R/N_A$. In other words, the last expression relates the average velocity to the temperature, *molar* mass and *gas constant*, while the second-to-last expression relates the average velocity to the temperature, *molecular* mass and *Boltzmann's constant.*

b) The most probable velocity is reached at the maximum of the probability distribution. Setting the derivative of $P(v)$ with respect to velocity equal to zero will give the maximum velocity. Recalling the values of the constants c_1 and c_2,

$$P(v) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-mv^2/2k_BT}4\pi v^2 = be^{-av^2}v^2$$

$$\frac{dP(v)}{dv} = be^{-av^2}(-2av)v^2 + be^{-av^2}2v = 0$$

after factoring out $be^{av^2}2v$, the above result implies that $1 - av^2 = 0$ when $v = v_{max}$ and so

$$v_{max} = \sqrt{\frac{1}{a}} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2RT}{M}}$$

c) The required velocities are obtained using the molecular weights of N_2 (28 g/mol) and H_2 (2 g/mol), as well as using the fact that in the SI unit system 1 J = 1 kg $(\text{m/s})^2$.

$$\langle v\rangle_{N_2} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314\text{J/mol}\cdot\text{K})(300\text{K})}{\pi(0.028\text{kg/mol})}} = 476\text{m/s}$$

$$\langle v\rangle_{H_2} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314\text{J/mol}\cdot\text{K})(300\text{K})}{\pi(0.002\text{kg/mol})}} = 1780\text{m/s}$$

$$v_{max}^{N_2} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314\text{J/mol}\cdot\text{K})(300\text{K})}{(0.028\text{kg/mol})}} = 422\text{m/s}$$

$$v_{max}^{H_2} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314\text{J/mol}\cdot\text{K})(300\text{K})}{(0.002\text{kg/mol})}} = 1580\text{m/s}$$

15. a)

$$\langle c_x^2\rangle = \int_0^\infty c_x^2 P(c_x)dc_x = a\int_0^\infty c_x^2 e^{-bc_x^2}dc_x$$

b) Using the integral table in Appendix B (and identifying the variable c_x by x) we obtain

$$a\int_0^\infty c_x^2 e^{-bc_x^2}dc_x = a\int_0^\infty x^2 e^{-bx^2}dx = \frac{a}{4}\sqrt{\frac{\pi}{b^3}}$$

c)

$$bc_x^2 = \frac{\frac{1}{2}mc_x^2}{k_BT} \qquad \text{so} \qquad b = \frac{m}{2k_BT}$$

d)

$$a = 2\sqrt{\frac{m}{2\pi k_B T}} = \sqrt{\frac{2m}{\pi k_B T}}$$

e)

$$\langle c_x^2 \rangle = \frac{k_B T}{m}$$

and therefore

$$\langle \varepsilon_x \rangle = \frac{1}{2} m \langle c_x^2 \rangle = \frac{1}{2} k_B T$$

as expected, given that the kinetic energy in the x-directions gives rise to a single quadratic term in the Hamiltonian!