Solutions to exercises in chapter 8

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1. **Diffusion of molecules**

   a) From the Einstein relation and the friction coefficient we obtain: $D = k_BT/f = k_BT/(8\pi\eta L)$. Numerically: $D = \frac{4pNnm}{8\pi 10^{-3}\pi 10^{-8}Pams} = \frac{410^{-21}Nm}{8\pi^2 10^{-11}Ns/m} = 1/2 \cdot 10^{-21}10^{10}m^2/s = 5 \cdot 10^{-12}m^2/s = 5(\mu m)^2/s$.

   b) We are looking at relative errors: $\sigma_D^2/D^2 = \sigma_\eta^2/\eta^2 + \sigma_L^2/L^2 = 0.01^2 + 0.01^2 = 2 * 0.01^2$. Hence: $\sigma_D/D = \sqrt{2} \cdot 0.01 = 0.014 = 1.4\%$. This gives: $\sigma_D \simeq 7 \cdot 10^{-14}m^2/s$

2. **Diffusion of molecules 2**

   a) We are looking for the time after which $\ell = \sqrt{\langle x^2 \rangle} = 10$ m. From the mean square displacement, we know $t = \langle x^2 \rangle/(6D) = \ell^2/(6D)$. Using the numerical values given: $t_{10m} = 100\text{m}^2/(96\text{mm}^2/\text{s})$ $= \frac{100}{96} \cdot 10^6$ s $\simeq 10^6$ s $\simeq 12$ days.

   b) Now we are doing the same as in a), but for a distance $\ell = 500\mu$ m $= 5 \cdot 10^{-4}$ m. Hence, $t_{500\mu m} = 25 \cdot 10^{-8}$ m$^2/(96 \cdot 10^{-6}$ m^2/s$) = \frac{25}{96} \cdot 10^{-2}$ s $\simeq 2.5$ ms.

   c) In both cases, the diffusivity is the only value with an uncertainty, where the relative error is $1/16 \simeq 6\%$. Therefore the times we obtain also have a relative error of 6%. Hence $\sigma_{t_{100m}} \simeq 0.7$ days and $\sigma_{t_{500\mu m}} \simeq 0.15$ ms.

3. **Diffusion and Brownian motion**

   a) $\langle \Delta x \rangle = \frac{\Sigma N_i \Delta x_i}{\Sigma N_i} = \frac{84-92+2\cdot 46-2\cdot 32+3\cdot 8-3\cdot 15+4\cdot 3-4\cdot 2+5\cdot 0-5\cdot 1}{400}\mu m = \frac{84-92+92-64+24-45+12-8-5}{400}\mu m = \frac{-2}{400}\mu m = -5nm$

   $\langle \Delta x^2 \rangle = \frac{\Sigma N_i \Delta x_i^2}{\Sigma N_i} = \frac{84+92+4\cdot 46+4\cdot 32+9\cdot 8+9\cdot 15+16\cdot 3+16\cdot 2+25\cdot 0+25\cdot 1}{400}\mu m^2 = \frac{84+92+184+128+72+135+48+32+25}{400}\mu m^2 = \frac{800}{400}\mu m^2 = 2\mu m^2$

   The diffusivity is defined via $\langle \Delta x^2 \rangle = 2Dt$, such that we have $D = \frac{\langle \Delta x^2 \rangle}{2t}$, where t is the observation time of 2 s. Thus we obtain a diffusivity of $D = 0.5\mu$ m^2/s.

   b) Einstein says: $D = k_BT/f$, or otherwise put $k_B = Df/T$, where $f = 6\pi\eta r$ is the friction coefficient of the droplet. Inserting this, as well as D from b), we obtain: $k_B = \frac{6\pi\langle \Delta x^2 \rangle \eta r}{2tT}$ or numerically: $k_B = \frac{6\pi 0.5\cdot 10^{-12}m^2/s\cdot 10^{-3}Pa\cdot s 0.4\cdot 10^{-6}m}{300K} = \frac{3\cdot 0.4\pi 10^{-21}J}{300K} = 0.4\pi 10^{-23}J/K = 1.26 \cdot 10^{-23}J/K$

   c) We have errors in η, T, t, r, that all enter the relation with an exponent of ± 1. We can therefore simply add all of the relative errors in squares, i.e. $r_{k_B} = \sqrt{r_\eta^2 + r_r^2 + r_T^2 + r_t^2}$. With the respective numerical values: $r_\eta = 0.05; r_r = 0.1; r_T = 0.01; r_t = 0.05$,we obtain $r_{k_B} = \sqrt{151}\% \simeq 12\%$. Our proper result for the Boltzmann constant fore is $k_B = 1.26(15) \cdot 10^{-23}J/K$, which is in good agreement with the official value of $1.38 \cdot 10^{-23}J/K$.

4. **Air pressure**

   a) If the fridge seals completely, the number of particles as well as the volume are constant. In that case, we have $p/T = const$ from the ideal gas law. This means that the pressure in the cooled down fridge is $p_2 = p_1T_2/T_1$, the pressure difference then is $\Delta p = p_1(1 - T_2/T_1)$. The force needed is the pressure difference multiplied by the area of the door, hence $F = \Delta pA = pbh(1 - T_2/T_1)$. Numerically: $F = 10^5$ Pa 2 m$^2(1 - 270/300) = 2 \cdot 10^5(1 - 0.9)$ N $= 2 \cdot 10^4$ N

   b) If the fridge does not seal properly, pressure and volume are constant, and we have $NT = const$ from the ideal gas law. Hence $\Delta N = N_1(1 - T_1/T_2)$. For a volume of $V = 1\text{m}^3$, we have initially $N_1 = \frac{pV}{k_BT_1} = \frac{10^5 J}{4\cdot 10^{-21}J} = 2.5 \cdot 10^{25}$ molecules in the fridge. With $(1 - T_1/T_2) = -0.1$, the number of molecules decreases by $\Delta N = 2.5 \cdot 10^{24}$. With $N_A = 6 \cdot 10^{23}$ molecules per mole this corresponds to roughly 4 moles disappearing out of the fridge.

5. **Heating a room**

   a) The internal energy is given by $U = \frac{f}{2}Nk_BT = \frac{f}{2}pV$, where we have used the ideal gas law ($Nk_BT = pV$). Neither pressure nor volume change in a room, such that U actually remains constant. The increase in temperature comes from a decrease in the number of particles (the room is not actually completely sealed).

   b) As pressure remains constant, we obtain the heat required using specific heat at constant pressure, i.e. $\delta Q = (1 + \frac{f}{2})Nk_B\Delta T = (1 + \frac{f}{2})pV\Delta T/T$ using the ideal gas law. Air is a bi-atomic gas, such that $f = 5$ and we end up with: $\delta Q = (7/2)pV\Delta T/T = \frac{7 \cdot 50 \cdot 10^5 Pam^3 3K}{2 \cdot 300K} = 1.7510^5$ J

   c) Errors are in p and V with relative errors of 2%, , i.e. the relative error in the heat required is $\sqrt{2} \cdot 2\% = 2.8\%$

6. **Thermal equilibrium**

   a) Temperature equalize in thermal equilibrium, i.e. $T_1' = T_2'$, for a fixed wall, the volumes must stay the same, i.e. $V_1' = V_1$ and $V_2' = V_2$. As volume and number of particles stay the same, the pressures have to change in response to the change in temperature, i.e. $p_1' > p_1$ and $p_2' < p_2$ if $T_1 < T_2$)

   b) The temperatures equalize (see a) $T_1' = T_2'$. Because of the moveable wall, so do the pressures, i.e. $p_1' = p_2'$. Hence the volumes have to change is response to these $V_1' > V_1$ and $V_2' < V_2$ if $T_1 < T_2$)

   c) Temperature equalize in thermal equilibrium, i.e. $T_1' = T_2'$, for a fixed wall, the volumes must stay the same, i.e. $V_1' = V_1$ and $V_2' = V_2$. As the wall is permeable to particles, the molecules distribute such that the pressures in both halves are equal.

7. **Thermal expansion**

   With $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}$ and $pV = Nk_BT$ we have: $\alpha = \frac{1}{V}\frac{\partial(Nk_BT/p)}{\partial T} = \frac{Nk_B}{pV} = \frac{Nk_B}{Nk_BT} = \frac{1}{T}$.

8. **Maxwell-Boltzmann distribution**

   (a) We obtain the maximum from taking the derivative and setting this zero. Taking the derivative of $P(v)$ gives: $dP/dv = const * (2vexp(-\frac{mv^2}{2k_BT}) + v^2exp(-\frac{mv^2}{2k_BT}) * (-\frac{mv}{k_BT})) = const * exp(-\frac{mv^2}{2k_BT})(2v - \frac{mv^3}{k_BT})$. Setting this zero means: $2v_{max} - \frac{mv_{max}^3}{k_BT} = 0$. Which can be solved to give: $v_{max} = \sqrt{2k_BT/m}$. This is the most probable speed of molecules in the gas.

   (b) The second moment of the distribution, $\langle v^2 \rangle = \int v^2P(v)dv$ is a measure of the width of the probability distribution, i.e. over what speed interval the speeds are distributed. For the Maxwell-Boltzmann distribution:

   $\langle v^2 \rangle = (\int v^2P(v)dv)/(\int P(v)dv)$

   $\langle v^2 \rangle = (\int v^4exp(-\frac{mv^2}{2k_BT})dv)/(\int v^2exp(-\frac{mv^2}{2k_BT})dv)$

   $\langle v^2 \rangle = \frac{k_BT}{m}(\int(\frac{mv^2}{k_BT})^2exp(-\frac{mv^2}{2k_BT})d(\sqrt{(\frac{mv^2}{k_BT})}))/(\int(\frac{mv^2}{k_BT})exp(-\frac{mv^2}{2k_BT})d(\sqrt{(\frac{mv^2}{k_BT})}))$

   $\langle v^2 \rangle = \frac{k_BT}{m}(\int x^4exp(-x^2/2)dx)/(\int x^2exp(-x^2/2)dx) = \frac{k_BT}{m}(3\sqrt{\pi/2})/(\sqrt{\pi/2}) = \frac{3k_BT}{m}$.

   To compare with a) we take the square root: $\sqrt{\langle v^2 \rangle} = \sqrt{3k_BT/m}$. This is larger by a factor of $\sqrt{3/2}$.

9. **Maxwell-Boltzmann distribution 2**

   a) At temperature T_1 we have $k = k_0 \exp(-\Delta E/(k_BT_1))$. We are looking for the temperature T_2 at which $k' = 2k = k_0 \exp(-\Delta E/(k_BT_2))$, hence $k'/k = 2 = \exp(-\Delta E/(k_BT_2) + \Delta E/(k_BT_1))$. Taking the log on both sides gives $\ln(2) = \Delta E/k_B(\frac{1}{T_1} - \frac{1}{T_2})$. This gives: $ln(2)k_BT_1/\Delta E = (T_2 - T_1)/T_2$. Solving for T_2 we have finally: $T_2 = T_1\frac{1}{1 - ln(2)k_BT_1/\Delta E}$ using the approximation $ln(2)k_BT/\Delta E = 0.07 \ll 1$ we can Taylor-expand this to find: $T_2 = T_1(1 + ln(2)k_BT_1/\Delta E)$. Numerically $k_BT_1/\Delta E = 0.1$, hence $T_2 = T_1(1.07) = 321K$.

b) Starting with the result of a): $T_2 = T_1(1+ln(2)k_BT_1/\Delta E)$. To get the uncertainty of T_2 we need the derivatives with respect to T_1 and ΔE respectively. These are: $\frac{\partial T_2}{\partial T_1} = 1 + 2ln(2)k_BT_1/\Delta E$ und $\frac{\partial T_2}{\partial \Delta E} = -ln(2)k_BT_1^2/\Delta E^2$, which gives for the uncertainty in T_2: $\sigma_{T_2}^2 = (1+2ln(2)k_BT_1/\Delta E)^2\sigma_{T_1}^2 + (ln(2)k_BT_1^2/\Delta E^2)^2\sigma_E^2 = (1+2ln(2)k_BT_1/\Delta E)^2\sigma_{T_1}^2 + (ln(2)k_BT_1/\Delta E)^2 r_E^2 T_1^2$. Numerically we have $r_E = 0.1$, $k_BT_1/\Delta E = 0.1$, $\sigma_{T_1} = 3K$ and $T_1 = 300K$, which gives: $\sigma_{T_2}^2 = (1.14)^2 9K^2 + 9(0.5 \cdot 0.01)0.01 \cdot 10^4 K^2 = 9(1.14^2 + 0.5)K^2 = 9 \cdot 1.8K^2$ and hence $\sigma_{T_2} = 3\sqrt{1.8}K \simeq 4.5K$.

10. **Specific heat**

(a) In a two-atomic ideal gas, there is kinetic as well as rotational energies. there are three directions for kinetic energy and two rotational axes for rotational energy, hence five degrees of freedom. Therefore according to equipartition, the total internal energy is $U = 5/2Nk_BT$. At constant volume there is no work being performed, hence a change in energy corresponds to a change in heat, such that the specific heat is given by $C_V = 5/2Nk_B$ or $C = 5/2R$ for one mole.

(b) For a process at constant pressure, there is not only heat but also work being performed. The first law of Thermodynamics stipulates for this: $\Delta U = \delta Q - \Delta W$. We know $\Delta U = f/2Nk_B\Delta T$ from equipartition and the ideal gas law tells us $\Delta W = p\Delta V = Nk_B\Delta T$ for the work performed. Taking all of this together gives for the change in heat: $\Delta Q = f/2Nk_B\Delta T + Nk_B\Delta T = (1 + f/2)Nk_B\Delta T$ and hence for the specific heat: $C_p = (1 + f/2)Nk_B$. For a mono-atomic gas $f = 3$, hence $C_p = 5/2Nk_B$.

11. **Elastic properties of DNA**

(a) The slope of the curve at large extension is roughly 70(5) pN/0.20(2)μm. This gives a spring constant of $k = 3.5(5) \cdot 10^{-4}$ N/m. The spring constant and the elastic modulus are connected via $E = kL/A$. Treating DNA as a cylinder with a diameter of 2.0(1) nm , we have $A = \pi$ nm^2 with an uncertainty of 10%. This finally gives $E = 3.5 \cdot 10^{-4} \cdot 1.6 \cdot 10^{-5}/\pi \cdot 10{-}18$ Pa = 1.75 GPa, where we have used a length of 16 μm.

(b) The relative error is given by the squared sum of the relative errors, i.e. $\sqrt{(5/35)^2 + (1/10)^2} = \sqrt{1/49 + 1/100} = 1/7\sqrt{1 + 49/100} = 1/7\sqrt{3/2} = \sqrt{3}/10 = 0.17$. This gives $\sigma_E = 0.3$ GPa.

(c) The initial slope is $k = 0.3(3)$ pN /1μ m. This gives $\xi_P = \frac{18 \cdot k_BT}{Lk} = \frac{18 \cdot 4pNnm}{16\mu m 0.3pN/\mu m} = 15nm$.

(d) Here we only need to consider the uncertainty in k, which is 100%. This means that k has a maximum value (twice the maximum error, i.e. value). The persistence length is inversely proportional to the slope, we can only give a lower bound (or minimal value) for ξ_P, which is about 10 nm. This means that any value larger than about 10 nm is compatible with the experiment. In a case like this, where the errors are very substantial, we can actually no longer use normal error propagation, since the assumption of small errors that are inherent in error propagation is actually not true. A more exact measurement of the persistence length of DNA gives 50 nm.

(e) Rearranging gives $E = \frac{16k_BT\xi_P}{\pi R^4}$. Inserting values and using $\pi/2 \simeq 1.6$ we find $E = \frac{5 \cdot \pi \cdot 4pNnm50nm}{\pi 1^4 nm^4} = \frac{50 \cdot 20 \cdot 10^{-12}}{1 \cdot 10^{-18}}$ Pa = 1 GPa.

12. **Packing of long molecules**

(a) A cell needs to be around twice the radius of gyration (Gaussian distribution 95% within 2 σ), i.e. $R_{cell} = 2R_G$. With $R_G^2 = \xi_P \cdot L/6$ we find: $R_{cell} = 2\sqrt{\xi_P L/6}$ or $R_{cell}^2/4 = \xi_P L/6$. Solving for L: $L = 3R_Z^2/(2\xi_P)$. Using the numerical values given: $L = 3 \cdot 5^2 \cdot 10^{-12}m^2/(2 \cdot 5 \cdot 10^{-8}m) = 3/2 \cdot 5 \cdot 10^{-4}$ m = 0.75 mm. With a base pair distance of 3.4 $\mathring{A} = 3.4 \cdot 10^{-10}$ m, this corresponds to $7.5/3.4 \cdot 10^6 \simeq 2 \cdot 10^6$ base pairs.

(b) The relative error in L is $r_L^2 = 4r_R^2 + r_\xi^2$ (R_{cell} enters squared, ξ_P linearly). With $r_R = 0.2$ and $r_\xi = 0.1$, this gives: $r_L^2 = 4 \cdot (0.2)^2 + 0.1^2 = 0.1^2(16 + 1) = 17 \cdot 0.1^2$. Hence: $r_L \simeq 0.4$ or 40%.

(c) With $E_{bend} = \pi ER^4L/(8r^2)$ and $\xi_P = \pi ER^4/(4k_BT)$ we obtain $E_{bend} = k_BT\xi_P L/(2r^2)$. Using $L = 2\pi r$ for a circle, we obtain: $E_{bend} = \pi k_BT\xi_P/r$. $\xi_P = 50(5)$ nm and $r = 5.0(5)$ nm, also ist $\xi_P/r = 10$. Furthermore, we know that $k_BT = 4pNnm$, to obtain: $E_{bend} = \pi k_BT\xi_P/r = \pi 4$pN nm 10 = $4\pi 10^{-12} \cdot 10^{-9} \cdot 10$ Nm $= 12 \cdot 10^{-20}$ J $= 1.2 \cdot 10^{-19}$ J.

(d) We have errors in ξ_P and r, both with a relative error of 10%. Hence the bending energy has a relative error of $(\sigma_E/E) = \sqrt{0.1^2 + 0.1^2} = \sqrt{2 \cdot 0.1^2} = \sqrt{2} \cdot 0.1 = 0.14$ or 14 % in other words, $\sigma_E \simeq 0.2 \cdot 10^{-19}$ J.

13. **Convection**

a) The ideal gas law says $N/V = p/(k_B T)$, so we obtain for ℓ: $\ell = \frac{k_B T}{2\pi d^2 p}$. Numerically: $\ell = \frac{4 \cdot 10^{-21} J}{2\pi 4 \cdot 10^{-20} m^2 10^5 Pa} = \frac{10^{-1} J}{2\pi 10^5 N} = \frac{10^{-6} m}{2\pi} \simeq 1.5 \cdot 10^{-7} m.$
b) With $\nu = \eta/\rho = \langle v \rangle \ell/3$, we have $\eta = \rho \langle v \rangle \ell/3$. Numerically: $\eta = 1 kg/m^3 500 m/s 1.5 \cdot 10^{-7} m/3 = 5 \cdot 1.5/3 10^{-5} kg/(ms) = 5 \cdot 0.5 10^{-5} Pas = 2.5 \cdot 10^{-5} Pas.$

c) The criterion for convection is: $Ra = \frac{g \Delta T d^3 \alpha}{\kappa \nu} 2000 = Ra_c$. With the values from a) and b), this gives a minimum layer thickness of: $d_{min} = (\frac{Ra_c \kappa \nu}{g \Delta T \alpha})^{1/3} = (\frac{Ra_c \kappa \nu T}{g \Delta T})^{1/3}$. Numerically: $d_{min} = (\frac{2 \cdot 10^3 2 \cdot 10^{-5} m^2/s 2 \cdot 10^{-5} m^2/s 300K}{10 m/s^2 10^{-2} K})^{1/3} = (\frac{24 \cdot 10^{-5} m^3}{10^{-1}})^{1/3} = (2.4 \cdot 10^{-3} m^3)^{1/3} = 2.4^{1/3} \cdot 10^{-1} m \simeq 13 cm.$

d) According to $d_{min} = (\frac{Ra_{krit} \kappa \nu T}{g \Delta T})^{1/3}$ all variables enter with a power of 1/3. We can therefore use relative errors for ease of calculation and obtain: $r_d^2 = (1/3)^2 (r_{Ra}^2 + r_\kappa^2 + r_\nu^2 + r_T^2 + r_{\Delta T}^2)$. Numerically: $r_{Ra} = r_\kappa = r_\nu = r_{\Delta T} = 0.1$ and $r_T = 0.01$. We thus neglect the error in T and get: $r_d^2 = (1/3)^2 (4 \cdot 0.1^2)$ or $r_d = 2/3 \cdot 0.1 \simeq 6.5\%$. This corresponds to $\sigma_d \simeq 1 cm$.