**Chemistry 410B** **Exam 3** **Spring 2009**

**Solutions**

1. **40 points.**

   (a) Which statements are true for a perfect blackbody? **Solution:** As $T$ increases, more more photons are radiated (and so more energy) at all frequencies, but the maximum shifts towards higher frequency. As $T$ increases:

      i. more energy is radiated at low frequency. $\boxed{\text{T}}$

      ii. more energy is radiated at high frequency. $\boxed{\text{T}}$

      iii. the most intense radiation shifts to longer wavelength. $\boxed{\text{F}}$ It shifts to higher *frequency.*

      iv. the photon number *and* average energy both increase. $\boxed{\text{T}}$

   (b) Add the periodic boundary conditions and calculate the energy of the Ising model lattice below.

$$\begin{matrix} + & - & - \\ - & + & - \\ - & - & - \end{matrix} \Rightarrow \begin{matrix} 6 & -4 & -4 \\ -4 & 6 & -4 \\ -4 & -4 & -4 \end{matrix} = \frac{-16D}{2} = \boxed{-8D}.$$

   (c) Two gas-phase samples, Ar ($\sigma = 36\,\text{Å}^2$, $m = 40\,\text{amu}$) and $C_2H_2$ ($\sigma = 72\,\text{Å}^2$, $m = 26\,\text{amu}$), have the same pressure and temperature. Given the values for Ar below, write the corresponding values for $C_2H_2$ in the same units.

| parameter | Ar | $C_2H_2$ | |
|---|---|---|---|
| $\rho\,(\text{m}^{-3})$ | $4.3 \cdot 10^{23}$ | $4.3 \cdot 10^{23}$ | depends only on $P$ and $T$ |
| $\lambda\,(\text{m})$ | $6.5 \cdot 10^{-6}$ | $3.2 \cdot 10^{-6}$ | inversely prop. to $\sigma$ |
| $\langle v_{AA} \rangle\ (\text{m}\,\text{s}^{-1})$ | 696 | 863 | prop. to $\sqrt{1/m}$ |
| $\gamma\,(\text{s}^{-1})$ | $1.1 \cdot 10^{8}$ | $2.7 \cdot 10^{8}$ | equal to $\rho \langle v_{AA} \rangle \sigma$ |

   (d) The diffusion constant for $SF_6$ in air is $0.150\,\text{cm}^2\,\text{s}^{-1}$ at 373 K. Find $r_{\text{rms}}$ after 1 hour. **Solution:** Use the Einstein diffusion equation:

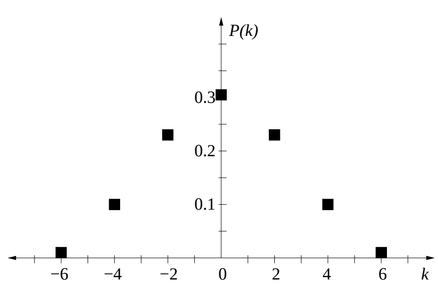
$$\langle r^2 \rangle^{1/2} = \sqrt{6Dt} = [6(0.150\,\text{cm}^2\,\text{s}^{-1})(3600\,\text{s})]^{1/2} = \boxed{57\,\text{cm}}.$$

2. Graph $\mathcal{P}(k)$ for **six** coin flips. **Solution:** Use the equation for the discrete distribution $\mathcal{P}(k)$ when $N$ is small. Because $N = 6$ is even, only even values of $k$ will be possible:

$$\mathcal{P}(k = \pm 6) = \frac{6!}{2^6\,6!\,0!} = \frac{1}{64} = 0.0156 \qquad \mathcal{P}(k = \pm 4) = \frac{6!}{2^6\,5!\,1!} = \frac{6}{64} = 0.0937$$

$$\mathcal{P}(k = \pm 2) = \frac{6!}{2^6\,4!\,2!} = \frac{15}{64} = 0.2344 \qquad \mathcal{P}(k = 0) = \frac{6!}{2^6\,3!\,3!} = \frac{20}{64} = 0.3125$$

As a check, these probabilities for all 7 possible values of $k$ add up to 1.



3. In an ideal gas sample, $PV$ is one measure of the energy content of the sample. If we set $PV_0 = \langle E_{\rm AB}\rangle$, where $\langle E_{\rm AB}\rangle$ is the average energy per collision, find an expression for the characteristic volume $V_0$ in terms of the mean free path and collision cross section. **Solution:** This is a mix-and-match algebra problem. In terms of our collision parameters, $P$ is related to $\rho$ which in turn determines $\lambda$, and $\langle E_{\rm AB}\rangle$ is equal to $3k_BT/2$. We can start from that and see where it leads us, keeping in mind that the final expression should depend on $\lambda$ and $\sigma$ only:

$$\begin{aligned} V_0 &= \frac{\langle E_{\rm AB}\rangle}{P} = \frac{3k_BT/2}{\rho RT/\mathcal{N}_A} = \frac{3k_BT/2}{\rho k_BT} \\ &= \frac{3}{2\rho} = \boxed{\tfrac{3}{2}\lambda\sigma}. \end{aligned}$$

4. Find an equation for the blackbody $\rho(\nu)$ assuming the energy is stored in quantum **rotations**. **Solution:** Starting from the general Eq. 15.25,

$$\rho(\nu) = \frac{8\pi\nu^2\langle\epsilon\rangle}{c^3},$$

we need the average rotational energy, rather than the average vibrational energy. To get that, we use the average value theorem and the partition function for rotation:

$$\begin{aligned} \langle\epsilon_{\rm rot}\rangle &= \int_0^\infty \mathcal{P}(J)\epsilon_{\rm rot}\,dJ = \frac{1}{q_{\rm rot}}\int_0^\infty (2J+1)e^{-BJ(J+1)/(k_BT)}\,BJ(J+1)\,dJ \\ &= \frac{B}{k_BT}\int_0^\infty e^{-Bx/(k_BT)}\,Bx\,dx = \frac{B^2}{k_BT}\left(\frac{1}{[B/(k_BT)]^2}\right) && \text{set } x = J(J+1) \\ &= \frac{B^2}{k_BT}\left(\frac{k_B^2T^2}{B^2}\right) = k_BT \end{aligned}$$

which we also could have predicted from the equipartition principle. Now we put this into the equation above for $\rho(\nu)$:

$$\rho(\nu) = \frac{8\pi k_BT\nu^2}{c^3}.$$

This diverges to infinity if you integrate over all frequencies, because the integral approximation to $q_{\rm rot}$ is not exact.