Section 2 – How Big is an Atom?

"Never trust atoms; they make up everything."

- Some 7th Grader, somewhere

During the rest of this course, we will often refer to *atoms*. The notion of the atom has been around for millennia, although a real understanding began only as recently as the nineteenth century with Dalton. Today, we define an atom as the smallest indivisible piece of a chemical element (hence the name, a-tomos = not sliceable). One of the recurring discussions we'll have will be how to determine the size of the atom. In this short section, we'll review some approximations.

The Oil Drop Experiment

You may have done this experiment in middle school. The surface of a pan of water is dusted with a fine powder. A very small drop of oil of known volume V_0 is dropped into the water and the oil spreads out over the surface of the water (oil and water don't mix).



The powder allows us to see the outline of the oil slick, usually a roughly circular shape, and measure its diameter, D. The oil itself forms a roughly cylindrical volume. Assuming that the volume of oil remains constant, we can easily calculate the thickness d of the film:

$$V_o = \pi \left(\frac{D}{2}\right)^2 d \rightarrow d = \frac{V_o}{\pi \left(\frac{D}{2}\right)^2}$$

The atoms of the oil can't be any larger than the value for d.

EXAMPLE 2-1

Suppose we do this experiment and find the initial diameter d of the spherical oil drop to be 0.5 mm. After dropping the oil, we measure the diameter of the oil slick D to be 140 mm. What is the upper limit on the size of the atoms in the oil?

The initial volume of the oil is

$$V_{o} = \frac{4\pi \left(\frac{d_{Drop}}{2}\right)^{3}}{3} = \frac{4\pi (0.5 \times 10^{-3}/2)^{3}}{3} = 6.54 \times 10^{-11} \text{m}^{3}.$$

The thickness of the oil slick is then

d =
$$\frac{V_o}{\pi \left(\frac{D_{Slick}}{2}\right)^2} = \frac{6.54 \times 10^{-11}}{\pi (0.14/2)^2} = 4 \times 10^{-9} \text{ m}$$

Hence, an 'atom of oil' must be smaller than about 4×10^{-9} m (40 Å) in diameter.^{1,2}

Avogadro's Number



There are a number of methods for determining Avogadro's number. This is one, although we will not evaluate it explicitly. Consider an electrolysis cell with two different metals. When a potential difference is applied across the electrodes in the proper polarity, Metal A ions will leave the electrode and be deposited onto the Metal B electrode. These ions each carry an integer number³ of fundamental electric charges (e)⁴ and thereby complete the circuit. The current and time are monitored, and at the end on the experiment, the amount of Metal A deposited on the Metal B electrode is measured. If we know the value of e and the bulk density of Metal A, we can determine the volume of one atom:

$$\frac{\text{Volume}}{\text{atom}} = \frac{\text{Volume}}{\text{kg}} \times (\#\text{kg transferred}) \times \frac{\text{valence} \times \text{fundamental charge}}{\text{atom}}$$
$$\times \frac{1}{\text{charge transferred}} \times \frac{\text{charge transferred}}{\text{current} \times \text{time}},$$

or, more succinctly,

 $\frac{\text{Volume}}{\text{atom}} = \frac{\text{valence} \times \text{e}}{\text{bulk density}} \times \frac{\text{mass trasferred}}{\text{current} \times \text{time}}$

EXAMPLE 2-2

The figure shows results from an experiment by Craig *et al.*⁵ Silver was deposited on a platinum electrode; the mass deposited was measured for several samples for different lengths of time. We see that the mass transferred *per* unit of charge is quite consistently 1.133×10^{-6} kg/coulomb.



¹ One Ångstrom (Å) is 10^{-10} m.

² You are probably aware that 'oil' is actually a *molecule*, and so comprises a number of atoms.

³ This number is the *valence number* for the atom.

⁴ We believe this for reasons better discussed in a Chemistry class.

⁵ Craig, D. Norman, James I. Hoffmann, Catherine A. Law, and Walter J. Hamer, 'Determination of the Value of the Faraday with a Silver-perchlorate Acid Coulometer, *Journal of Research* **64A** p381.

The bulk density of silver is 10,490 kg/m³ and the valence is thought to be +1. Then, the average volume *per* atom would be

$$\frac{\text{volume}}{\text{atom}} = \frac{1 \times (1.6 \times 10^{-19} \text{ C})}{10490 \text{ kg/m}^3} \times 1.133 \times 10^{-6} \text{kg/C} = 1.73 \times 10^{-29} \text{m}^3$$

If we assume the atoms are spheres, then the diameter is given approximately⁶ by

$$d = \sqrt[3]{\frac{6 V}{\pi}} = \sqrt[3]{\frac{6 (1.73 \times 10^{-29})}{\pi}} = 3.21 \times 10^{-10} \text{ cm} \simeq \frac{3.2 \text{ Å}}{3.2 \text{ Å}}$$

HOMEWORK 2-1

Suppose we know from other means that the diameter of a copper atom is 2.6Å. Having the FCC structure, the atoms themselves occupy only 0.74 of the available volume.⁷ An electrolysis experiment with copper sulfate (CuSO₄) reveals that 0.295 grams of copper is deposited *per* hour at a constant current of 0.25 amps. What is the valence of copper? The bulk density of copper is 8920 kg/m³.

We can return to Example 2-2 knowing that silver also has an FCC structure to get a better estimate. Then,

$$d = \sqrt[3]{\frac{6(0.74)V}{\pi}} = \sqrt[3]{\frac{6(0.74)(1.73 \times 10^{-29})}{\pi}} = 2.90 \times 10^{-1} \text{ cm} \simeq \frac{2.9 \text{ Å}}{2.9 \text{ Å}} ,$$

which agrees well with the currently accepted value.

EXAMPLE 2-3

Find the packing factor of the FCC structure. Let L be the length of the edge of the cube. We'll assume that the atoms are hard spheres that touch each other. FCC has an eighth of an atom at each corner and a half atom at the center of each face. A slice along one of the cube faces would look like the diagram on the right. A diagonal along the face would then be four sphere radiuses:



⁶ Why approximately? We're assuming <u>here</u> that the atoms are like stacked cubes of volume 1.73×10^{-29} m³; a sphere of the same volume would actually have a diameter <u>bigger</u> than the length of such a cube. The atoms are perhaps better represented by spheres sitting in those stacked boxes, in contact with their neighbors, and as such, there are some spaces between the spheres that are empty. How much is empty depends on the crystal structure of the material. There are fourteen different crystal structures, three of which are cubic. A *simple cubic* structure (SC) has an atom at each corner of the cube, or rather, an eighth of an atom at each corner and one in the center of the cube, and the face centered cubic structure (FCC) has an atom at each corner and one at the center of each face.

⁷ This number is called the *atomic packing factor*. If we pack together a bunch of spheres, there will be some space left between them. So, for example, in a 1 m³ block of copper, the atoms themselves occupy only 0.74 m^3 .

$$\sqrt{2}L = 4R \quad \rightarrow \quad R = \frac{L}{2\sqrt{2}} \; .$$

Altogether, there are eight eighth spheres (corners) and six half spheres (faces) for a total of four spheres contained in the cube. Then, the packing factor is the ratio of sphere volume to cube volume:

$$PF_{FCC} = \frac{4\left(\frac{4\pi}{3}R^3\right)}{L^3} = \frac{16\pi}{3} \frac{\left(\frac{L}{2\sqrt{2}}\right)^3}{L^3} = \frac{16\pi}{3(16\sqrt{2})} = 0.74$$

EXERCISE 2-1

Find the packing factor of the BCC structure.

HOMEWORK 2-2

Find the packing factor for the simple cubic structure. Again, assume the atoms are hard spheres that touch. HINT: a slice along one of the cube faces would look like this:



The Van der Walls Equation

Another method used to determine the size of the atom comes from chemistry. Recall that the ideal gas law is

$$PV = nRT$$
,

with P the absolute gas pressure, V the volume of the container, and T the absolute temperature. The amount of gas is measured in moles, n. R, the universal gas constant, is actually just $N_A k_B$. This relationship is valid when the density of the gas is fairly low. However, at much higher densities, some corrections are necessary. The *Van der Waals equation* modifies the pressure and volume terms.⁸ Of lesser interest to us now is the pressure term. There is a weak, usually attractive force between the molecules due to an electric dipole interaction. This causes the gas to be slightly denser in its interior than at the container's surface, where the pressure is measured; so, the gas's pressure is actually a bit higher than the measured value.

$$P \rightarrow P + a \left(\frac{n}{V}\right)^2$$
.

⁸ There are of course even more complex models of gas behavior, such as the Beattie-Bridgeman equation, the Benedict-Rubin-Webb equation, and the Strobridge equation.

This postulated correction is proportional to the square of the density, n/V, of the gas.⁹ The term is squared because each particle (the number of which is proportional to n/V) must interact with all of the other particles (almost exactly proportional to n/V), giving us a number of interactions proportional to $(n/V)^2$.

The volume correction is more pertinent to this discussion. In our ideal gas equation discussion, we assumed that the particles were point masses and did not interact with each other. Essentially, the entire volume V was available to each of the particles in our container. However, as more particles are put in the container, less space is available to the other particles to move about. This effectively reduces the volume of the container available to each particle by NV_o (= nN_AV_o), where V_o is the volume of one gas particle. So, we now have

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - n N_A V_o) = nRT$$

Now, we look at the PV diagram of a very dense gas, fit the parameters a and V_o , and the approximate volume of the particle pops out. The diameter of such a particle, if assumed to be spherical, is then, as above,

$$d = \sqrt[3]{\frac{6V_o}{\pi}}$$

EXAMPLE 2-4

The figure shows the P-V diagram for N_2 at 130K.^{10,11} This temperature was chosen because it's the lowest temperature for which N_2 remains a gas across this range of pressures for which data were available. The red line is a best fit curve using the Van der Waals relationship:

 $a = 0.122 \text{ Pa m}^2/\text{mole}^2$

$$V_o = 5.48 \times 10^{-29} \text{ m}^3$$
.



If we divide the volume equally between the two nitrogen atoms, the diameter from the equation above is then approximately 3.7×10^{-10} m or ~ 4 Å. This of course doesn't take into account any volume associated with the separation of the atoms.

 $^{^{9}}$ If there are N particles, each must interact with each of the remaining N-1 particles so that there are N(N-1) interactions. For large N, this is darn close to N².

¹⁰ National Bureau of Standards Cryogenic Engineering Laboratory, Boulder, Colorado. The graph is reproduced in Van Wylen, Gordon J., and Richard E. Sonntag, <u>Fundamentals of Classical Thermodynamics</u>, John Wiley and Sons, New York (1978) p392. Note that nitrogen is diatomic.

¹¹ Although the horizontal axis is labeled 'specific volume,' it is the volume *per* mole of gas.

The	table below	lists the	fitting pa	rameters	and ap	proximate	diameters	for a	variety	of g	gases. ¹²
I've	chosen the n	oble gase	es becaus	e they co	mprise	only one at	tom.				

Gas	a (m ⁶ Pa/mole ²)	$V_{o}(m^{3})$	Diameter (Å)
Helium	0.003412	3.935x10 ⁻²⁹	4.2
Neon	0.02107	2.837x10 ⁻²⁹	3.8
Argon	0.1345	5.345x10 ⁻²⁹	4.7
Krypton	0.2318	6.605x10 ⁻²⁹	5.0
Xenon	0.4194	8.476x10 ⁻²⁹	5.5

We can do this a bit more mathematically if we notice that, for the lowest possible temperature for which the gas remains a gas, T_c , there is an inflection point (where the first and second derivatives are zero) in the PV curve. Then, rewriting the Van der Waals equation as

$$P = nRT(V - n N_A V_o)^{-1} - an^2 V^{-2}$$
,

we note that, at that critical point,

$$P_{C} = nRT_{C}(V_{C} - n N_{A} V_{o})^{-1} - an^{2}V_{C}^{-2} ,$$

$$\frac{dP}{dV}\Big|_{C} = -nRT_{C}(V_{C} - n N_{A} V_{o})^{-2} + 2an^{2}V_{C}^{-3} = 0$$

,

and

$$\left. \frac{d^2 P}{dV^2} \right|_C = +2nRT_C(V_C - n N_A V_o)^{-3} - 6an^2 V_C^{-4} = 0 .$$

¹² CRC Handbook of Chemistry and Physics, 71st edition p 6-47.

Solving these last two equations, we find that

$$V_{o} = \frac{1}{3N_{A}} \left(\frac{V}{n} \right)_{C}$$

Let's check this with our nitrogen data. The critical specific volume is 0.01 liters/mole; about after converting units, the volume *per* molecule is then 5.5×10^{-30} m³. If we divide this volume between the two atoms, we obtain a diameter of about 1.8 Å.

EXERCISE 2-2

Do the math that results in the relationship above for V_o.

HOMEWORK 2-3

Regard the graph¹³ of the critical

Pressure (atm) 74 73 72 0.003 0.004 0.006 0.005

Specific Volume (liters/mole)

Isotherms of CO₂

-31.01 C

31.32 C

-31.52 C

32.05 C

isotherm (blue) for CO₂. Calculate the approximate diameter of a carbon or oxygen atom (assume that they are about the same size) from the relationship above for V_o.

77

76

75

X-Rays

X-rays, highly energetic electro-magnetic waves, can be generated in a number of ways. Typically, in a mid-sized laboratory, X-rays are produced by accelerating electrons through an electric potential difference V into a metal target, which produces radiation in two distinct ways (see the figure to the right). The first type of radiation is called *Brehmsstrahlung*, or 'braking radiation,'

and is due to the fact that accelerating charges emit radiation. The electrons give up their kinetic energy as X-rays as they hit the target and come to a stop. The broad distribution of emitted wavelengths is due to the fact that not all electrons arrive at the target with the same velocity, or they lose energy in some



¹³ A. Michels, B. Blaisse and C. Michels, 'The Isotherms of CO₂ in the Neighbourhood of the Critical Point and Round the Coexistence Line,' Proc. R. Soc. Lond. A 160 pp358-375.

other way. The sharp cut off at the short wavelength (high energy) end of the spectrum is of course because even the fastest electrons can emit only the energy they possess as kinetic energy. This in turn depends on the acceleration voltage of the tube (V_1 , V_2 , and V_3 in the figure).

The *characteristic line* wavelengths depend on the specific metal being used as the target. In much the same way that gases emit characteristic spectra when excited, so too do metals.¹⁴ We'll discuss the reasons for this later. We can determine the wavelengths λ of these X-ray lines by observing the diffraction pattern created as they pass through, for example, a pair of very narrow slits; values for the wavelength range from about 2 Å to 0.2 Å, generally smaller with increasing atomic number.

Adding a filter to the emitted X-rays can remove, to some degree, parts of the emission spectrum. For example, a nickel filter will remove most of the radiation just above the Ka line of a copper target tube.

We can make use of the characteristic wavelength X-rays to probe crystals. Crystals are thought to have atoms arranged in lattice-like structures with regular spacing between adjacent atoms. If so, we might expect to observe diffraction effects as we did for visible light. Let's consider a *simple cubic* structure, one with an identical atom at each corner of many cubes of side L. The value of L would then be an upper limit on the diameter of the atoms. The figure shows a schematic cross section of the arrangement. The method we will use to determine the conditions for constructive interference is similar to that of Huygens we used for reflection. The X-rays are scattered off each atom, essentially in all directions, but only in some directions will there be constructive interference and therefor a strong outgoing wave.

Consider two adjacent atoms on the surface of a crystal, separated by distance L. The incoming X-ray is incident¹⁵ at angle θ_1 and the strong outgoing ray (constructive interference) is at angle θ_2 . Since the two points at each end of each of the blue lines are in phase, we should consider the distances marked d_1 and



d₂. In order for constructive interference to occur, the difference in the lengths of the paths of the two rays $|d_1 - d_2|$ must be an integer number of wavelengths, n:

$$|\mathbf{d}_1 - \mathbf{d}_2| = \mathbf{n}\lambda$$

where

$$d_1 = L \cos \theta_1$$
 and $d_2 = L \cos \theta_2$.

¹⁴ We will see later that the K α line is a 2 \rightarrow 1 *transition* while the K β line is a 3 \rightarrow 1 transition. The L α line is the 3 \rightarrow 2 transition. We'll discuss what a transition is later.

¹⁵ Note that the angles are measured from the surface to the direction of the beam, not from the normal, as was done with light waves.

So,

$$L(\cos \theta_1 - \cos \theta_2) = n\lambda, \quad n = 0, \pm 1, \pm 2, \dots$$



For the case of n = 0, the two angles are equal.

At the same, since X-rays are expected to penetrate into the material, so there must also be constructive interference from the waves scattered by atoms in adjacent lower layers.

Let's consider only the special case of $\theta_1 = \theta_2 = \theta$. Then, $d_1 = L \sin \theta$ and $d_2 = L \sin \theta$. For constructive interference, we require $d_1 + d_2$ to be an integer number, m, of wavelengths so that

 $L(\sin\theta + \sin\theta) = m\lambda, \quad m = 1, 2, 3, \dots$

This renders the second required condition as

$$2L\sin\theta = m\lambda$$
 m = 1, 2, 3, ... when n = 0

This is referred to as *Bragg diffraction*. Often, X-ray measurements are performed on a *swing-arm goniometer*.¹⁶ This device maintains the sample in an orientation such that the incoming and detection angles are equal, *i.e.*, it detects only the n = 0 diffraction peaks. So, let's not worry about other possibilities. Due to the construction of the diffractometer, data are recorded in terms of 2 θ , rather than θ .



EXAMPLE 2-5

It would be nice to be able to present sample data for a single crystal of an element in the *simple cubic* structure. Unfortunately, the only such element is polonium, which is highly radioactive and has a propensity to turn rapidly into lead. Needless to say, such data would



be difficult to obtain.



Instead, we'll look at a slightly more complicated structure. From *Laue pattern diffraction*,¹⁷ we know that niobium forms a *body*-

¹⁶ There are other methods, of course.

¹⁷ Laue patterns are extremely difficult to analyze; we'll leave this for your X-ray diffraction course in graduate school.

centered cubic (BCC) structure. This arrangement comprises a cube of side length L with an atom at each corner and another at the center of the cube. Alternatively, we can imagine two parallel layers of atoms a distance L/2 apart, but with one layer offset at 45° to the other. Niobium (100) shows a strong first order (m = 1) diffraction of Cu Ka X-rays (1.541 Å) at $2\theta = 55.5^{\circ}$.¹⁸ The length of the side of a cubic cell of niobium is then

$$2\left(\frac{L}{2}\right)\sin\theta = m\lambda,$$
$$L = \frac{m\lambda}{\sin\theta} = \frac{(1)(1.541)}{\sin(27.75^{\circ})} = \frac{3.31 \text{ Å}}{3.31 \text{ Å}}.$$

Consequently, the center-to-center distance between nearest neighbors is halfway across the diagonal of the cube, $0.5 \times 3^{1/2} \times 3.31$ Å $\simeq 3$ Å apart.¹⁹ We can be pretty confident that niobium atoms have a diameter no larger than this value. Other metals give similar results.

HOMEWORK 2-4

Let's consider polonium. A Po crystal in the (100) orientation has planes separated by 3.34Å. If the $W_{K\alpha}$ line (0.021 nm) is incident on this face, at what angles should there be (Bragg) diffracted rays? Find only the four smallest angles.



Thermal Conductivity of Gases

Let's consider a gas of N particles contained in a volume V_o with temperature T. From our previous discussion of the kinetic theory of gases, the particles are zipping around, bouncing off the walls of the container and each other, with an r.m.s. speed given by

$$\mathrm{K} = \frac{1}{2}\mathrm{m}\mathrm{v}_{\mathrm{rms}}^2 = \frac{3}{2}\mathrm{k}_{\mathrm{B}}\mathrm{T}\,.$$

¹⁸ Pan,T.J., Y.Chen, B.Zhang, J.Hu, and C.Li, 'Corrosion behavior of niobium coated 304 stainless steel in acid solution,' *Applied Surface Science* **369** p320.

¹⁹ This is the distance across the 3-dimensional diagonal using the Pythagorean theorem.

You may remember that the Boltzmann's constant $k_B = R/N_A$. We'd like to estimate the *mean free path* of a particle, *l*, that is, how far does it travel, on average, between collisions?²⁰ Let's assume that the particle is a sphere of diameter d. As one such moves through space from one collision to the next, it sweeps out a cylindrical volume of $l\pi(d/2)^2$. Now, we're going to use a bit of a trick. In order for our particle to collide with another particle, their centers must come to within two radiuses (= d) of each other. So, we're going to make the moving particle have an effective radius of d and make all the other particles into stationary points.²¹ So, the volume swept out by the moving particle will be

$$V = l \pi d^2.$$

which in turn we should expect to be roughly equal to the particle's 'share' of the overall volume, V_0/N :

$$\frac{V_o}{N} = l \, \pi d^2$$

Next, we need to estimate the mean free path. There are a number of ways to do this; we'll make use of the thermal conductivity of the gas.²²





Let's make our container a rectangular box of length L and cross sectional area A. The left side is held at a temperature T_H and the right at T_C . The other sides are insulated. You may remember that the rate of thermal energy transfer from one end to the other is given by

$$H = \frac{\delta Q}{dt} = \frac{\sigma A}{L} |\Delta T|, \quad (*)$$



²⁰ Obviously, some will travel long distances and some short; we'll assume that they all travel the average distance.

²¹ This derivation makes use of many approximations, but in the end, our answer will be of the correct order of magnitude.

²² The following discussion is based loosely on that in Tipler, Paul A., Foundations of Modern Physics, Worth Publishers, New York (1969) pp 86-90.

where σ is the thermal conductivity of the gas.²³ How is energy transported from one end to the other? The particles on the left side are 'hotter,' and so possess more kinetic energy and of course move more quickly than the 'cooler' particles on the right. Some of the more energetic left-hand particles move to the right, carrying energy, and an equal number of right hand particles move to the left, but they carry less energy, so there is a net transfer of energy to the right, *i.e.*, from hot to cold.²⁴



Let's look at this in more detail. We'll pick a location

 x_o along the x axis and place an imaginary boundary there for the particles to pass across. The particles that will cross from the left without any additional collisions should come from a layer of width Δx (= *l*, the mean free path) adjacent to and to the left of the boundary, and the particles that will move to the left come from a layer of width Δx adjacent to the boundary on the other side. We might expect about half of the particles in each layer will cross the boundary, since for each layer, about half will be traveling to the right and half to the left.²⁵ So, the number of particles crossing the boundary in each direction should be one half times the density of particles times the volume containing the particles, or about

$$\frac{1}{2} \left(\frac{\mathrm{N}}{\mathrm{V_o}} \right) (\mathrm{A} l) .$$

The kinetic energy carried by all of these particles will be:²⁶

$$\frac{\mathrm{NA}\,l}{\mathrm{2V_o}} \,\mathrm{K}(\mathrm{x_o}-l)\,.$$

to the right and

$$\frac{N A l}{2V_{o}} K(x_{o} + l)$$

to the left. Since l is expected to be a small number, we can expand these expressions about x_0 :

$$\frac{\mathrm{NA}\,l}{2\mathrm{V_o}}\mathrm{K}(\mathrm{x_o} + \Delta \mathrm{x}) \simeq \frac{\mathrm{NA}\,l}{2\mathrm{V_o}} \left[\mathrm{K}(\mathrm{x_o}) + \frac{\mathrm{dK}}{\mathrm{dx}}\Big|_{\mathrm{x_o}}\Delta \mathrm{x} + \cdots\right]$$

²³ This is analogous to Ohm's relationship for electricity: $I = \frac{\sigma A}{L} \Delta V$.

²⁴ Remember, everything discussed here is 'on average.'

²⁵ The fraction should be even less that one half, since the particles are also moving in the y and z directions.

²⁶ Here, $K(x_0 - l)$ means that the kinetic energy as a function of where along the x-axis we're looking. It's not K times $(x_0 - l)$.

to obtain, when $\Delta x = l$,

$$\frac{\mathrm{NA}l}{\mathrm{2V_o}} \left[\mathrm{K}(\mathrm{x_o}) - \frac{\mathrm{dK}}{\mathrm{dx}} \Big|_{\mathrm{x_o}} l \right] \quad \text{and} \quad \frac{\mathrm{NA}l}{\mathrm{2V_o}} \left[\mathrm{K}(\mathrm{x_o}) + \frac{\mathrm{dK}}{\mathrm{dx}} \Big|_{\mathrm{x_o}} l \right],$$

respectively. The net transfer of energy across our boundary at x_0 will be the difference of these expressions:

$$-2 \left. \frac{\mathrm{N} \mathrm{A} l}{2 \mathrm{V}_{\mathrm{o}}} \frac{\mathrm{d} \mathrm{K}}{\mathrm{d} \mathrm{x}} \right|_{\mathrm{x}_{\mathrm{o}}} l = \left. \frac{\mathrm{N} \mathrm{A} l^2}{\mathrm{V}_{\mathrm{o}}} \left| \frac{\mathrm{d} \mathrm{K}}{\mathrm{d} \mathrm{x}} \right|_{\mathrm{x}_{\mathrm{o}}} \right| \,.$$

Then, we have that

$$\frac{\mathrm{d}K}{\mathrm{d}x} = \frac{\mathrm{d}K}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{3}{2}k_{\mathrm{B}}\frac{\mathrm{d}T}{\mathrm{d}x},$$

so that the energy transferred is

$$\frac{3\mathrm{N}\,\mathrm{A}\,l^2\,\mathrm{k}_{\mathrm{B}}}{2\mathrm{V}_{\mathrm{o}}}\left|\frac{\mathrm{d}\mathrm{T}}{\mathrm{d}\mathrm{x}}\right|_{\mathrm{x}_{\mathrm{o}}}\right|\,.$$

The time required for such an exchange to take place is the travel time for the gas particles to move the distance *l* from their last collision to the boundary, or $t = l/v_{rms}$, so that the <u>rate</u> of energy transfer will be

$$H = \frac{\frac{3N A l^2 k_B}{2V_o} \left| \frac{dT}{dx} \right|_{x_o} \right|}{\frac{l}{v_{rms}}} = \left(\frac{3}{2} \left(\frac{N}{V_o} \right) l v_{rms} k_B \right) A \left| \frac{dT}{dx} \right|_{x_o} \right|$$

Comparing this result term by term with the equation above (*) and assuming that the temperature gradient is constant (*i.e.*, $dT/dx = \Delta T/L$) indicates that the thermal conductivity σ of the gas should be

$$\sigma = \frac{3}{2} \left(\frac{N}{V_o} l \right) k_B v_{rms} = \frac{3}{2} \left(\frac{1}{\pi d^2} \right) k_B \sqrt{\frac{3k_B T}{m}} .$$

So,

$$d = \left(\frac{27}{4\pi^2} \frac{k_B^3}{\sigma^2} \frac{T}{m}\right)^{1/4} \, .$$

Finally, let's calculate the sizes of some atoms:

Gas	Thermal Conductivity at 300K	Diameter		
	$(W/mK)^{27}$	(Å)		
Helium	0.157	2.4		
Neon	0.050	2.8		
Argon	0.026	3.3		
Krypton	0.012	4.0		
Xenon	0.0055	5.3		

HOMEWORK 2-5

Use these results and work backward to find the mean free path lengths l of helium and xenon at 300K. Assume a pressure of one atm.

The Wrap-up

We've looked at a number of methods for determining an upper limit to the size of the atom, which appears to on the order of several Ångstroms. What we didn't do is show evidence that atoms actually exist. This is usually credited to investigations of what we now call *Brownian motion*, by Lucretius, Ingerhousz, Brown, Einstein, and Perrin. Although Einstein's explanation of Brownian motion is perhaps a bit too advanced for this class, it also leads to an estimate of the size of atoms. Otherwise, we'll leave this to your Chemistry instructors.

In subsequent sections of these notes, we'll return to the determination of the size of the atom.

Exercise 2-1 Soln

BCC has an eighth sphere at each corner of the cube and one at the center, for a total of two spheres. The diagonal across the cube, $\sqrt{3}L$, would be four radiuses. So,

$$\sqrt{3}L = 4R \quad \rightarrow \quad R = \frac{\sqrt{3}L}{4}$$

$$PF_{BCC} = \frac{2\left(\frac{4\pi}{3}R^3\right)}{L^3} = \frac{8\pi}{3} \frac{\left(\frac{\sqrt{3}L}{4}\right)^3}{L^3} = \frac{8\pi 3\sqrt{3}}{3(64)} = 0.68$$

Exercise 2-2 Soln

²⁷ Lide, David R., <u>Handbook of Chemistry and Physics 71st ed.</u>, CRC Press Boca Raton (1990) p6-148.

Re-arrange the first and second derivatives evaluated at the critical point:

$$nRT_{C}(V_{C} - n N_{A} V_{o})^{-2} = 2an^{2}V_{C}^{-3}$$

and

$$2nRT_C(V_C - n \; N_A \; V_o)^{-3} = 6an^2 V_C^{-4} \;\; . \label{eq:relation}$$

Divide the first equation by the second:

$$\frac{nRT_{C}(V_{C} - n N_{A} V_{o})^{-2}}{2nRT_{C}(V_{C} - n N_{A} V_{o})^{-3}} = \frac{2an^{2}V_{C}^{-3}}{6an^{2}V_{C}^{-4}} ,$$

$$\frac{V_{C} - n N_{A} V_{o}}{2} = \frac{V_{C}}{3} ,$$

$$n N_{A} V_{o} = \frac{V_{C}}{3} ,$$

$$\frac{V_{O} = \frac{1}{3N_{A}} \left(\frac{V_{C}}{n}\right) .$$