What is the Physical Significance of Avogadro's Number?

The modern statement that a mole of gas contains a number of gas atoms or molecules equal to Avogadro's number, denoted by N_A, is based on a long history of ideas. The enormous size of N_A, $6.02214179(30) \times 10^{23}$ (see NIST CODATA, 2007) is difficult to appreciate. It is a testament to the incredibly small size of atoms, of the order of several cubic angstroms ($10^{-8} cm$). This length unit, the angstrom, denoted by Å, is a clue to the size of N_A. One cm^3 is 10^{24} Å^3. [A new value for N_A has just been published {Andreas et al., *Physical Review Letters* **106**, 030801 (2011)} and has a smaller uncertainty: $6.02214078(18) \times 10^{23}$. However the one standard deviation error bar interval for the NIST value and the new value do not overlap, *op cit*. figure 5, and look at the sixth decimal place.]*

Avogadro's number tells us the size difference between the *objective* microscopic world of the atomic elements and the *subjective* macroscopic world of humans. One could argue that the human size scale also is somehow set by fundamental processes, and therefore is also *objective*, but for now it suffices to simply note that the two scales are the atomic scale and the human scale. Thus a mole of ideal gas at $0^o C$ and one atmosphere of pressure has a volume of $22.414 \ldots$ liters according to the ideal gas laws. A liter is $10^3 \ cm^3$, or a cube of $10 \ cm$ on a side. This is about $4 \ inches$ on a side. Thus, a volume of 27 liters is roughly a cubic foot and has about 20 percent more gas molecules in it than are in one mole.

The connection between the microscopic world and the macroscopic world has fascinated humankind for ages. That a microscopic atomic world exists was sensed long ago but it was only during the early twentieth century that the reality of the atomic world and an atom's objective size were explicitly determined. This determination *simultaneously* fixed the size of atoms and the magnitude of Avogadro's number. Before these measurements, it was possible that an atom had a radius of order, say, $10 - 100 \ nm$ and was still invisible to an optical microscope. Correspondingly, Avogadro's number would have been orders of magnitude smaller.

The basic idea about how to determine these two quantities was seen by Josef Loschmidt and following this idea Albert Einstein worked out the details in his doctoral thesis in 1905. The thesis is titled "A New Determination of Molecular Dimensions" and was eventually published in *Annalen der Physik* **19**, 289 (1906). There are two ingredients to the Einstein-Loschmidt method of determination of atomic sizes and Avogadro's number. The first is a hydrodynamic calculation of the effect on shear viscosity of adding a small amount of solute to a pure solvent. Einstein assumed that the solute molecules were simple spheres that were much larger than the solvent molecules so that the solvent could be treated hydrodynamically as a continuous fluid without concern for its molecular structure. Using "stick" boundary conditions on the small spheres Einstein was eventually able to derive (in spite of several computational errors) the formula

$$\eta^* = \eta \times \left(\frac{5}{2} n \frac{4\pi}{3} a^3 \right)$$

in which η is the shear viscosity of the pure solvent and η^* is the viscosity of the solution that contains n solute molecules per unit volume, each of radius a. Using the concept of the mole, the mass density of the solute in grams per unit volume, ρ, the molecular weight of a solute molecule, m, Einstein replaced n by (in his book, *Investigations on the Theory of the Brownian Movement* [Dover Pub. Inc., 1956, New York], originally published in German in 1926, Einstein has the coefficient ratio erroneously upside down on p. 60 but correctly on p. 57)

$$n = \frac{\rho}{m} N_A$$

yielding the result

$$\eta^* = \eta \times \left(\frac{5}{2} N_A \frac{\rho}{m} \frac{4\pi}{3} a^3 \right)$$

Einstein originally got the factor of 5/2 wrong because of improper implementation of the hydrodynamic boundary value problem. However, this much of Loschmidt's

idea could have been performed by many scientists at the time and after a series of corrections Einstein got it right.

Einstein's seminal contribution was the second part, a detailed account of Brownian motion, although at the time (1905) he did not recognize his result by this name. He calculated the diffusion constant, D, of one of the solute molecules (spheres) in the solvent. He got the result (assuming spheres of radius a)

$$D = \frac{k_B T}{6\pi\eta a}$$

in which k_B is Boltzmann's constant and T is the solvent temperature. From statistical mechanics, and in particular from the calculation of the ideal gas laws using these methods, it is known that

$$R = N_A k_B$$

in which R is the gas constant so that the diffusion constant can be expressed by

$$D = \frac{R}{N_A} \frac{T}{6\pi\eta a}$$

Einstein's formula for the diffusion constant connects the microscopic world, k_B, to a macroscopically measured quantity, D. These days we use the stochastic Ornstein-Uhlenbeck formulation (Langevin equation) to describe the emergence of Einstein's formula and cite the formula as an example of the fundamental microscopic-macroscopic connection called the *fluctuation-dissipation relation*. The denominator of D was computed by Stokes in 1851 using hydrodynamics and in 1969 Fox and Uhlenbeck showed that a sphere moving in a fluctuating hydrodynamic fluid obeys Langevin's equation.

The viscosity result, η^*, and the diffusion constant result, D, provide two equations in two unknowns, N_A and a! Real gas measurements gave a value for R,

and Einstein determined N_A and a from Graham's measurements of the viscosity of sugar-in-water solutions compared to that of pure water getting, in April of 1905

$$a = 6.2 \times 10^{-8} cm$$
$$N_A = 3.3 \times 10^{23}$$

Graham's solutions were more concentrated than allowed by the assumptions made in Einstein's calculations and this accounts for some of the discrepancy with modern values. Using measurements of Thovert and of Hosking, Einstein reported in January of 1906 revised values of

$$a = 4.9 \times 10^{-8} cm$$
$$N_A = 6.56 \times 10^{23}$$

Jean Perrin did the first really accurate measurements in 1909 and received the Nobel prize for this and related work in 1926. This really clinched the reality of molecules.

These results make clear the feasibility of determining Avogadro's number by measurement of two quantities that represent the two separate length scales, the microscopic and the macroscopic. Today we can measure the gas constant R and the Boltzmann constant k_B and deduce Avogadro's number from their ratio. The Boltzmann constant can be acquired from stochastic considerations and measurements of microscopic fluctuations although with great difficulty if high precision is desired.

In 1988 Michael R. Moldover measured R using the acoustic resonator method. He did this largely on his own time and with his own money. Using acoustic eigenmodes in a spherical cavity it is possible to determine R with greatly increased precision (see http://nvl.nist.gov/pub/nistpubs/sp958-lide/339-343.pdf .) The value he obtained is still the one quoted in the NIST CODATA tables*

$$R = 8.314472(15) \frac{J}{mol - K}$$

It is noteworthy to observe that the NIST CODATA value for k_B is determined by dividing the R value above by the NIST CODATA value for N_A, and is not independently obtained. From the ratio we get

$$k_B = \frac{8.314472(15)}{6.02214179(30) \times 10^{23}} \frac{J}{K} = 1.3806503(25) \times 10^{-23} \frac{J}{K}$$

Compare this with the NIST CODATA value*

$$k_B = 1.3806504(24) \times 10^{-23} \frac{J}{K}$$

To implement the calculation of Avogadro's constant from the gas constant and Boltzmann's constant we need an independent measurement of Boltzmann's constant. Using Einstein's ideas about Brownian motion and his formula for the diffusion constant it is possible to make measurements that are of low precision. Using video microscopy of Brownian motion (just as Perrin had done), Nakroshis et al. published results in *American Journal of Physics* **71** pp. 568-573 (2003). They obtained

$$k_B = 1.413(40) \times 10^{-23} \frac{J}{K}$$

The precision is low but at least the one standard deviation error bar overlaps the much more precise NIST CODATA value above.

There is an electrical analog to the Brownian motion method (fluctuation-dissipation relation) for determining Boltzmann's constant directly. This involves electric current fluctuations and electrical resistance. A very modern version of this was published in 2009 by Benz et al. (*Comptes Rendus Physique* **10** pp. 849-858 (2009)) The precision in the NIST CODATA table, as given above, is 1.7×10^{-6}. Using this electrical method (a quantum-voltage-calibrated Johnson noise thermometer) Benz et al. claim they can do as well.

Another approach to measuring Boltzmann's constant is the laser spectroscopy method of C. Lemarchand et al. (*International Journal of Thermophysics* **31** pp. 1347-1359 (2010)). They report the result

$$k_B = 1.380716(51) \times 10^{-23} \frac{J}{K}$$

This has a precision of only 3.7×10^{-5}. There may be improvements in this method that yield greater precision.

For the present the relative uncertainty in the values of Boltzmann's constant obtained by direct measurement are greater than the NIST CODATA value obtained from the gas constant and Avogadro's number, each of which is much more precisely known. However, the new value for Avogadro's number implies a new value for Boltzmann's constant

$$k_B = \frac{8.314472(15)}{6.02214078(18) \times 10^{23}} \frac{J}{K} = 1.3806505(25) \times 10^{-23} \frac{J}{K}$$

which differs only in the noise.

These considerations have implications for efforts to redefine the kilogram. A recent review of the two most prominent methods, the watt-balance and the silicon sphere, has emphasized the advantages to the silicon sphere approach (V. V. Khruschov, *Measurement Techniques* **53** pp. 583-591 (2010)). This method is also known as the Avogadro method and highlights the importance of the considerations in this note.

This history, some of which is very recent, does not explain how the NIST CODATA value for N_A is so precise. This is a result of basing its value on quantities determined by atomic physics and not by the fluctuation-dissipation relation in hydrodynamic or electrical systems. Remarkably, in spite of depending on single ion measurements in a Penning trap, there is still a fundamental connection between the microscopic and macroscopic worlds nevertheless [D. L.

Farnham et al., *Physical Review Letters*, **75** pp. 3598-3601 (1995)]. The key identity is given by

$$N_A = \frac{A_r(e)M_u}{m_e}$$

in which M_u is the exactly defined *molar mass constant* $0.001\ kg/mol$, $A_r(e)$ is the *electron relative atomic mass* which is measured but is dimensionless, and m_e is the *electron rest mass* that is determined indirectly from other measured quantities. Instead of using SI units I use the cgs system of units common in quantum and relativistic physics. Thus $M_u = gm/mol$, and m_e can be obtained from the Rydberg energy as follows. The Rydberg energy scale is defined by

$$R_y \equiv \frac{e^2}{2a_0} = \frac{(4.80320427(12) \times 10^{-10}\ esu)^2}{2 \times 0.52917720859(36) \times 10^{-8}\ cm} = 13.6056923(12)\ eV$$

in which we have used the *charge of the electron*, e, and the *Bohr radius*, a_0, defined by

$$a_0 \equiv \frac{\hbar^2}{m_e e^2}$$

in which *Planck's constant*, h, appears devided by 2π, $\hbar$. Elimination of the Bohr radius between these two expressions yields

$$m_e = \frac{2\hbar^2 R_y}{e^4} = 9.10938215(45) \times 10^{-28}\ gm$$

   The leaves determination of the electron relative atomic mass, $A_r(e)$. This is determined using a Penning trap, a clever arrangement of a uniform magnetic field and a quadrupolar electric field configured in such a way that an ion can be trapped in three dimensions. Because of its charge the ion undergoes cyclotron motion in the magnetic field that permits measurement of the relative cyclotron frequencies of two ions. For the electron the other ion is chosen to be C^{6+}, the completely

ionized carbon atom. The carbon-12 isotope is used for reasons that follow. The IUPAC definition of atomic weight is:

An atomic weight (relative atomic mass) of an element from a specified source is the ratio of the average mass per atom of the element to 1/12 of the mass of an atom of ^{12}C.

From the measurement using C^{6+} it is possible to compute the relative atomic mass of neutral C by adding the relative atomic mass of 6 electrons and subtracting a factor accounting for the binding energy of the electrons in the atom. The ratio of cyclotron frequencies gets converted into the electron relative atomic mass. The explicit assumption is made that the electron relative atomic mass is the same for the free ion as it is for the atomically bound electrons. This is the place in the argument at which the connection between these clearly microscopic considerations and macroscopic considerations occurs. By definition,

the mass of Avogadro's number of carbon-12 atoms, non-interacting and in their ground state, is exactly 12 gm.

Since the measurement, including the corrections just mentioned, of $A_r(e)$ yields

$$A_r(e) = 5.485799111(12) \times 10^{-4}$$

the mass of a mole of electrons is $A_r(e)M_u$. Thus Avogadro's number is given by the ratio at the beginning of this section

$$N_A = \frac{A_r(e)M_u}{m_e} = \frac{5.485799111(12) \times 10^{-4}\,\frac{gm}{mol}}{9.10938215(45) \times 10^{-28}\,gm}$$

$$= 6.02214181(30) \times 10^{23}/mol$$

The *definition* of mass in terms of a mole of carbon-12 atoms brings in the macroscopic scale. The Penning trap yields the electron relative atomic mass, the mass ratio of an electron and a carbon-12 atom, but not the mass in grams of a single electron. The mass of an electron, as given earlier in terms of the Rydberg energy, leads to the expression (cgs units)

$$N_A = \frac{A_r(e)M_u e^4}{2\hbar^2 R_y}$$

The molar mass constant is defined, the electron relative atomic mass is measured, the electron charge is measured, the Rydberg energy is measured and Planck's constant is measured. In recent proposals to fix exactly more of the fundamental constants some scientists want to fix exactly Avogadro's number and others want to fix exactly Planck's constant (see the Khruschov reference above). Obviously you can't fix both independently if you respect the measured values of the other quantities. It will be a challenge to see if direct measurements of the gas constant and of Boltzmann's constant will ever be precise enough to yield a value for Avogadro's number as precise as the current NIST CODATA value obtained with a Penning trap.

If the silicon sphere method for defining the kilogram is adopted, it may prove desirable to replace the definition of the gram in terms of carbon-12 with one based on silicon-28 (twice before we have changed standards, from a proton, originally, to an atom of oxygen-16, and then to carbon-12). Then it would be required to re-measure the electron relative atomic mass from Penning trap measurements that compare an electron to an Si^{14+} ion. Whether the same high precision is possible in this case remains to be seen.

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* New values for N_A, R and k_B have been published as the 2010 NIST CODATA values. Thes values are

$$R = 8.3144621(75)\frac{J}{mol-K}$$

$$N_A = 6.02214129(27) \times 10^{23}/mol$$

$$k_B = 1.3806488(13) \times 10^{-23} \frac{J}{K}$$

While the N_A value is only slightly different the R value is nearly an order of magnitude more precise. Once again, dividing the quoted R value by the quoted N_A value yields the new k_B value with the quoted uncertainty.

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