1 How to measure the number of molecules, I

Up until the first years of the twentieth century, there were still physicists who didn't believe in the atomic theory. Their main point was that there wasn't an experiment to actually count the number of atoms (or molecules) in a sample of matter. Everything macroscopic measurement seemed to be related to some product of the number of particles and a microscopic value, so that if the number of particles is changed by a factor while the microscopic quantity changes by the inverse of that factor, the overall result doesn't change, A very simple example is this. Consider a sample of material, supposedly consisting of N molecules, each of mass m. If the mass of this sample is measured (a macroscopic measurement), the result would be $(N\,m)$. From this, one cannot find the values of both N and m. You can multiply N by one half, and m by two (a smaller number of bigger molecules) and the overall mass doesn't change.

A somewhat less trivial example is the refractive index of a gas sample. For materials without a strong magnetic property (which are most of the materials, essentially only ferromagnetic materials have strong magnetic properties) the refractive index n is related to the (electric) permitivity ε through

$$n = \sqrt{\frac{\varepsilon}{\varepsilon_0}}, \tag{1}$$

where ε_0 is the permitivity of the vacuum. ε is related to the susceptibility χ, through

$$\varepsilon = \varepsilon_0\,(1 + \chi). \tag{2}$$

So,

$$n = \sqrt{1 + \chi}. \tag{3}$$

The susceptibility measures the response of mater to an electric field: When an electric field is applied to the matter, the positive and negative charges of the matter ares lightly displaced. Positive charges move in the direction of the electric field, while negative charges move in the opposite direction. The result is an electric dipole. When a charge q is displaced from a change $(-q)$ by a displacement vector $\boldsymbol{\Delta}$, the electric dipole $\boldsymbol{p}$ is

$$\boldsymbol{p} = q\,\boldsymbol{\Delta}. \tag{4}$$

For small electric fields, the displacement of the charges are proportional to the electric field. hence so is the produced electric field. The result is for any molecule there is a polarizability γ, so that the electric dipole $\boldsymbol{p}$ induced in the molecule with the electric field $\boldsymbol{E}$ satisfies

$$\boldsymbol{p} = \varepsilon_0\,\gamma\,\boldsymbol{E}. \tag{5}$$

If there are N such molecules in a volume V, the total elecetric dipole would be N times the above. So $\boldsymbol{P}$, the total electric dipole per volume, would be

$$\boldsymbol{P} = \varepsilon_0 \, \frac{N\,\gamma}{V}\, \boldsymbol{E}. \tag{6}$$

The susceptibility is defined through the following.

$$\boldsymbol{P} = \varepsilon_0 \, \chi \, \boldsymbol{E}. \tag{7}$$

So,

$$\chi = \frac{N\,\gamma}{V}. \tag{8}$$

N can be written in terms of N_{mol} (the number of moles), and N_{A} (the Avogadro number):

$$N = N_{\text{A}}\, N_{\text{mol}}. \tag{9}$$

So,

$$\chi = \frac{N_{\text{mol}}}{V}\, (N_{\text{A}}\, \gamma). \tag{10}$$

I haven't proved why this susceptibility is related to the refractive index the way claimed above. One can find the proof in textbooks on electromagnetism. But for now, I'm going to just use this. As it is seen, the susceptibility is a function of the product $(N\,\gamma)$. So measuring the refractive index, and hence determining the susceptibility, one can find only the product $(N\,\gamma)$, not both N and γ. Alternatively, (N_{mol}/V) is the molar density, which is a macroscopic quantity. Determining the susceptibility,a nd knowing the molar density, gives only the molar polarizability $(N_{\text{A}}\,\gamma)$, not both the Avogadro number and the (molecular) polarizability.