Revised Calculation of the Translational Fluctuation Effect in Gaseous Dielectrics

J. H. Van Vleck

Articles you may be interested in

Diffusion effects of hydrogen bond fluctuations. II. From the short to the long time regime in the translational dynamics of water
J. Chem. Phys. **91**, 1191 (1989); 10.1063/1.457192

Diffusion effects of hydrogen bond fluctuations. I. The long time regime of the translational and rotational diffusion of water
J. Chem. Phys. **91**, 1179 (1989); 10.1063/1.457191

Calculation of Loudness: 1961 Revision
J. Acoust. Soc. Am. **33**, 838 (1961); 10.1121/1.1936822

Revised Calculation of Deformation Twinning Systems
J. Appl. Phys. **29**, 1771 (1958); 10.1063/1.1723046

The Dielectric Strength of Gaseous Fluorocarbons
J. Appl. Phys. **21**, 203 (1950); 10.1063/1.1699635

Revised Calculation of the Translational Fluctuation Effect in Gaseous Dielectrics

Even in gases, the Clausius-Mossotti ratio is not quite independent of density. Hence if one writes

$$\frac{\epsilon-1}{\epsilon+2} V = P_0 \left[1 + \frac{\lambda P_0}{V} + \omega \left(\frac{P_0}{V} \right)^2 + \cdots \right], \quad (1)$$

where P_0 and V are the molar polarization and volume, the correction term $\lambda P_0/V$ can be detected at high pressures. Owing to the close approach of molecules at collisions, the values of λ are much larger than they would be were the atoms uniformly spaced, so that the phenomenon is sometimes called the "translational fluctuation effect." At the end of a previous article,[1] I calculated λ for a classical model of superposed harmonic oscillators and rigid dipoles. For the special case of nonpolar molecules my formula reduced to

$$\lambda P_0 = (8\pi L\alpha^2/3a^3)[1 + \tfrac{1}{2}\alpha a^{-3} + 2\alpha^2 a^{-6} + \cdots]. \quad (2)$$

Here α is the polarizability and a is the distance of closest approach. Kirkwood[2] had previously obtained the formula

$$\lambda P_0 = (8\pi L\alpha^2/3a^3)(1 + A/3bRT), \quad (3)$$

where A and $b = 2\pi L a^3/3$ are the constants of the equation of state $p = RT/(V-b) - A/V^2$.

Eq. (3) does not agree with the leading member of (2), obtained by disregarding the part of (2) in square brackets. Consequently I stated that I believed Kirkwood's van der Waals correction, i.e. the last factor of (3), was "extraneous," primarily because of the fact that in the way I made my own calculations the polarization forces were already included in the model, so that it would be redundant and erroneous to introduce in addition an inverse sixth power attractive term, as Kirkwood did. However, my criticism of his work was incorrect, as his computations were made in a different way. He points out to me that the van der Waals correction in (3) is really a part of the a^{-9} term of (2) a fact not very clear in his paper. He further notes that if higher terms in the solution of his Eq. (20) are included, then (3) becomes

$$\lambda P_0 = (8\pi L\alpha^2/3a^3)(1 + \tfrac{1}{2}\alpha a^{-3} + \alpha^2 a^{-6} + A/3bRT + \cdots), \quad (4)$$

and that (4) agrees with (2) if one uses the value

$$A = 2\pi k T L^2 \alpha^2/a^3 \quad (5)$$

of A appropriate to classical harmonic oscillators. Eq. (5) also, of course, applies to quantum-mechanical oscillators if their characteristic frequency ν is small compared with kT/h. In the other limit $h\nu \gg kT$ the quantal value of A is

$$A = \tfrac{1}{2}\pi h\nu\alpha^2 L^2/a^3. \quad (6)$$

Now the harmonic model is being used to depict the induced polarization associated with electronic motions, and so (6) rather than (5) should be employed. Also, since ν is large, (6) is considerably greater than (5), and when (6) rather than (5) is substituted, (4) ceases to agree with (2). The question immediately arises as to whether (4) or (2) is then the better approximation. It immediately becomes apparent that I was wrong in supposing that in considering the translational fluctuation effect it is immaterial whether the oscillators are handled in a classical or quantal way, as is the case in so many problems. To settle the point definitely, I have therefore revised

my calculations, treating the oscillators by quantum mechanics. Inasmuch as only the λ correction term in (2) is desired, only two atoms at a time need be considered in the expansion of the partition function, and accurate quantization of a system of two oscillators is possible with dipole-dipole interaction and an applied electric field, since even with these complications the energy remains a quadratic function of the harmonic displacements, permitting the use of normal coordinates. The procedure is described in somewhat simplified form in a paper by London[3] and need not be explained in detail here. London did not have the terms due to the applied field, as he was not considering dielectric constants, but they are handled by a simple shift in origin. Also the calculations can be made to include polar molecules by treating the rotational coordinates by means of classical theory, and regarding them as fixed parameters insofar as they enter in the quantization of the oscillators. These approximations are fully allowable inasmuch as the frequency of end-over-end rotation is small compared both with kT/h and with the oscillator frequency. Not all the spatial averaging given in my previous paper need be repeated, as it is possible to see from the multiplicative way in which the oscillator functions enter, just how the formulas must be modified in going from the classical to quantal case. It is finally found that if $h\nu \gg kT$, then

$$\lambda P_0 = (8\pi L\alpha^2/9a^3)(3+2y)(1 + \tfrac{1}{5}\Omega a^{-6} + \Omega^2 a^{-12}/10 + \cdots)$$
$$+ (4\pi L\alpha^3/225a^6)(15 + 10y + y^2)^2$$
$$\times (3+y)^{-1}(1 + \tfrac{1}{2}\Omega a^{-6} + \cdots) \quad (7)$$
$$+ (4\pi L\alpha^4/225a^9)[(15 + 10y + y^2)(60 + 60y + 8y^2)$$
$$\times (3+y)^{-1} - 50(3+2y)],$$

where $y = \mu^2/\alpha kT$ and $\Omega = \tfrac{3}{4}h\nu\alpha^2/kT$. The expression $\tfrac{2}{3}kT\pi L^2\Omega$ is the same as the van der Waals constant A if the molecule is nonpolar and if in addition squares and higher powers of Ω are overlooked. These conditions are basic both to (5) and (6), which alike neglect the effect of the permanent dipole moment μ and cubes of α. If these conditions are met, Eq. (7) is valid for all values of the ratio $h\nu/kT$ if Ω is defined as $3A/2\pi L^2kT$. In (7), all terms in a^{-9} have been included, and also, unless y is very large probably the most important terms in a^{-12} and a^{-15}. For the special case $y=0$ of nonpolar molecules, (7) reduces, except for higher members, to (4). Thus Kirkwood's results are entirely correct, but formula (7) is, of course, more general, in that it includes polar molecules.

Unfortunately use of (7) rather than my former Eq. (20) makes the agreement with experiment worse in the case of NH_3. Namely, the computed value of λ (with London's[3] estimate of ν) becomes about 0.7 rather than 0.4, whereas the observations of Keyes and collaborators give $\lambda = 0.3$.

The considerations of the present note in no way affect the discussion of liquids and solids which constituted all but the final section of my previous article. The coefficient of a^{-9} was not involved, and so no distinction between classical and quantal results came into play.

Princeton University,
  Princeton, N. J.,
  November 11, 1937.
J. H. Van Vleck

[1] J. H. Van Vleck, J. Chem. Phys. 5, 556 (1937).
[2] J. G. Kirkwood, J. Chem. Phys. 4, 592 (1936).
[3] F. London, Zeits. f. physik. Chemie 11B, 222 (1930); Trans. Faraday Soc. 33, 8 (1937).