

On the Role of DipoleDipole Coupling in Dielectric Media

J. H. Van Vleck

Citation: [The Journal of Chemical Physics](#) **5**, 556 (1937); doi: 10.1063/1.1750074

View online: <http://dx.doi.org/10.1063/1.1750074>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/5/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Confinement effects on dipole–dipole interactions in nanofluids: The role of equilibrium fluctuations](#)
J. Chem. Phys. **134**, 114519 (2011); 10.1063/1.3567757

[The role of the dipole–dipole interaction in the energy transfer process in aromatic solutions](#)
J. Chem. Phys. **67**, 4735 (1977); 10.1063/1.434599

[The Role of DipoleDipole Interactions in the Critical Behavior of Ferromagnetic Materials](#)
AIP Conf. Proc. **10**, 822 (1973); 10.1063/1.2947028

[Infrared Spectrum and Dipole—Dipole Coupling in Crystalline Cyanogen](#)
J. Chem. Phys. **39**, 2274 (1963); 10.1063/1.1701429

[Influence of DipoleDipole Coupling on Specific Heat of a Paramagnetic Salt](#)
J. Chem. Phys. **32**, 1573 (1960); 10.1063/1.1730966



The presence or absence of the states at 260 cm^{-1} has little effect on the heat capacity up to 40°K . Consequently the experimental results are actually only a test of the presence of the energy level at 77 cm^{-1} and the assumption that its statistical weight is twice that of the lowest level. The agreement between the direct experimental heat capacity values and those calculated from spectroscopic data is conducive to acceptance of the

interpretation given. An assumption that the statistical weights are equal leads to a radical disagreement. The fact, shown by the measurements, that the heat capacity curve of the salt between 3° and 10°K does not depart appreciably from the simple type of pattern produced by the elastic vibrations in the crystal lattice shows that the separation of the two lowest states (double-level) must be less than 1 cm^{-1} .

JULY, 1937

JOURNAL OF CHEMICAL PHYSICS

VOLUME 5

On the Role of Dipole-Dipole Coupling in Dielectric Media

J. H. VAN VLECK

Harvard University, Cambridge, Massachusetts

(Received May 13, 1937)

The mathematical treatment of dipole-dipole coupling in my previous article on magnetism applies with but little modification to the electric case. Because of fluctuation effects, the use of the usual Lorentz local field $E + 4\pi P/3$ and of the Clausius-Mossotti formula cannot be justified except as a first approximation valid at low density. Consequently one need not accept the C-M prediction that polar liquids should exhibit the electric analogue of ferromagnetism. A Gaussian approximation, or better still, a formula based on Onsager's field would never allow ferromagnetism. Consequently the hypothesis of hindered rotation, as in the theories of Fowler and Debye, may not be necessary to explain the absence of spontaneous polarization, as well as the non-occurrence of much saturation

curvature in strong applied fields. It is a weakness of their theory that this hypothesis cannot consistently be employed both for such purposes and to explain discontinuities in dielectric constants and specific heats at lower temperatures (e.g., 100° in HCl). It is surprising that the Clausius-Mossotti formula works so exceedingly well as it does in nonpolar liquids, since it is theoretically valid at high densities only for an artificial model of harmonic oscillators which cannot be regarded as an accurate representation of the induced polarization. The calculations of Kirkwood on the translational fluctuation effect, causing deviations from the C-M expression in gases, are extended to include polar molecules, and agree adequately with recent measurements of Keyes and collaborators on NH_3 .

1. INTRODUCTION—ADAPTATION OF OUR PREVIOUS CALCULATIONS TO THE ELECTRIC CASE

IN an article in a preceding issue of this journal (henceforth called l.c.¹), I considered the influence of dipole-dipole coupling on the paramagnetic susceptibility, and found it unimportant except at very low temperatures. On the other hand, due to the fact that the dipole moment, expressed in appropriate units, is usually much larger in the electric than in the magnetic case, this coupling affects the dielectric constant of a polar substance even at room temperatures. The calculations of l.c. apply to electric susceptibilities with but little change. There is also the corresponding specific heat which is

due to electric dipole-dipole coupling, but which we shall not discuss explicitly since the bearing on experiment is meager owing to overshadowing by other specific heats. In the particular case of susceptibility due entirely to permanent dipoles, the detailed development of the partition function in $1/T$ is almost identical with that given in Sections 3-4 of l.c. if $g^2\beta^2 J(J+1)$ everywhere be replaced by the square of the permanent dipole moment μ of the molecule. There is, however, the simplification that the various components of electric dipole moment commute in matrix multiplication. Hence the noncommutation correction factor x given in (55) of my previous paper¹ is replaced by unity. Also the exchange terms involving the v 's are to be suppressed, as exchange coupling does not have a simple aligning effect on the electric moment. This statement does not

¹ J. H. Van Vleck, *J. Chem. Physics* **5**, 320 (1937); referred to throughout as l.c. In Eq. (57), z should be replaced by z' .

mean that ultimately the exchange forces cannot affect the orientation of the moment, but this influence will be at such small distances that even electrostatic forces cannot be represented by a dipole-dipole potential. In other words, at too great concentrations higher order poles, with exchange ramifications, can come into play. The problem then becomes one of hopeless complexity, involving what Fowler calls "cooperative phenomena," and we must content ourselves with the consideration of ordinary dipole-dipole coupling.

As compared with the magnetic case perhaps the most important difference of all is in the practical definition of the susceptibility. We saw that in magnetic measurements the "experimental susceptibility" was the ratio of moment to the field strength *before* insertion of the test body. However, in determinations of dielectric constants, the drop of potential across the test body is recorded, and so the mean or macroscopic field E actually inside the specimen is measured directly. The experimental susceptibility is conveniently defined as the ratio of the polarization P per unit volume to E and is the same as the theoretical definition of the susceptibility in electromagnetic theory. There is consequently no need of an analogue of a demagnetizing correction and if the body is isotropic with evenly spaced similar atoms, the local field is simply $E + 4\pi P/3$, where E is known. Hence in adapting the calculations of l.c. we can replace H_0 by E and take Φ everywhere equal to $4\pi/3$ since the part of (43) of l.c. arising from demagnetizing effects is to be omitted. This is an obvious improvement, as Φ then ceases to be shape dependent.

Clausius-Mossotti formula. According to the usual Lorentz theory, the effect of dipole-dipole coupling is equivalent to taking the local field to be $E + 4\pi P/3$. Then

$$(\epsilon - 1)E/4\pi = P = N\gamma(E + 4\pi P/3), \quad (1)$$

where γ is the polarizability per atom and N is the number of atoms per cc. One thus has immediately the Clausius-Mossotti formula

$$\frac{M}{\rho} \frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi L\gamma}{3}. \quad (2)$$

The Avogadro number is denoted by L , and M is the molecular weight. The important feature of (2) is that its right side is a constant independent of the density ρ . The usual Langevin-Debye formula gives $\gamma = \alpha + \mu^2/3kT$, where μ is the permanent dipole moment of a molecule, and α represents the effect of the induced polarization. Thus Eq. (1) can also be written

$$\epsilon - 1 = 3q\theta/(T - q\theta), \quad (3)$$

where

$$\theta = 4\pi N\mu^2/9k = 4\pi\tau/9, \quad q = 1 + (3\alpha kT/\mu^2). \quad (4)$$

In polar media, most of the electric susceptibility arises from the permanent dipoles, and the factor q embodying the effect of induced polarization may be replaced by unity without serious error.

2. POLAR LIQUIDS AND SOLIDS

As stressed in l.c., the usual Lorentz derivation² of (1) and hence (2, 3) is based on essentially electrostatic methods and consequently cannot be regarded as rigorous. Instead the problem should be treated as one in statistical mechanics. Our previous paper¹ contains, we believe, the first general kinetic derivation of (2) or (3). However, these formulas are obtained only if either: (a) θ is small compared to T so that in the development of the partition function as a series in $1/kT$ only terms of the first order in the dipole-dipole interaction need be retained, or if (b) the results of this first approximation be extrapolated to higher approximations by a procedure which is comparable to assuming that all states of the same crystalline spin have the same energy in the Heisenberg theory of ferromagnetism. The assumption (b) is, however, necessary to yield (2-3) in liquids and solids, where θ is comparable with T , and certainly (b) is not rigorous. If instead of (b) one extrapolates the results of the second approximation by a procedure analogous to using a Gaussian distribution of energies in Heisenberg's theory, one has³

² Cf. H. A. Lorentz, *The Theory of Electrons*, note 54.

³ In the case $q=1$ of no induced polarization, Eq. (5) is the same as (56) of l.c. when adapted to the electric case as explained in Section 1. Eq. (5) is also valid when the induced moment is included, provided it is represented by the harmonic oscillator model. The proof of (5) under these conditions is obtained in the following way as a by-product to our analysis of the translational fluctuation effect in Section 5 of the present paper. The expression $2\alpha^{(2)}\chi_0^{-1}kT$

$$\epsilon - 1 = \frac{3\theta q}{T - \theta q + (9Q\theta^2/16\pi^2 T)}. \quad (5)$$

The quantity Q is dimensionless and is defined as

$$Q = 2N^{-2} \sum_j r_{ij}^{-6}, \quad (6)$$

where r_{ij} is the distance between atoms i and j and the summation is over all atoms j in the crystal. The values of Q are 16.8 and 14.4, respectively, for simple and face-centered cubic lattices, while Q becomes $2(4\pi/3)^2 = 35.1$ for a continuous distribution analogous to that usually assumed in classical theory. (Cf. Eqs. (20) and (60) of l.c.) Another possible way of extrapolating the second approximation is by means of Onsager's formula⁴

$$\frac{\epsilon - 1}{\epsilon + 2} - 4\pi \left(\frac{N\alpha}{3} + \frac{N\mu^2}{9kT} \right) = (f - 1) \frac{4\pi N\mu^2}{9kT}, \quad (7)$$

$$\text{with } f = \frac{3\epsilon(n^2 + 2)}{(2\epsilon + n^2)(\epsilon + 2)}, \quad \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N\alpha}{3}. \quad (7a)$$

Onsager obtained his formula on the ground that the Lorentz field is not really the best electrostatic model and ought to be modified to allow for the "back action" of the medium on the dielectric. This distinction is perhaps most easily comprehended by consulting Fig. 1 of l.c. In the Onsager model as we use it, the cavity is supposed to equal the mean molecular volume in size. In Fig. 1, it is drawn the same size in the Lorentz picture, as is allowable since (except for the Onsager reaction effect) the field at the center of a cavity in a uniformly polarized medium is independent of its diameter. For purposes of deriving the Lorentz formula, the cavity is usually considered very much larger, so as to embrace a considerable number of molecules, whose effect on the central molecule is

in (82) of l.c. represents the effect of the term α in (6^a) of l.c. (type $i=k, j=l$) and so must equal the quantity $\lambda P_0/V$ calculated in our later Section 5 when Q is specialized to $32\pi^2/9$ in (5), when only terms of order $1/a^3$ are retained in (20), and when $4\pi a^3/3$ is taken equal to $1/N = V/L$. Namely, with these restrictions it is easily seen that there is no distinction from a formal standpoint between a calculation with the continuum model of regularly spaced atoms, and one on the translational fluctuation effect. The result (5) then follows from (82) of l.c. on using the value of λP_0 given in (20) of the present paper and on noting that $\alpha^{(2)}$ is proportional to Q .

⁴ L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

supposed to vanish on the average if there is spherical symmetry. The gist of the Onsager modification is that the latter supposition is not legitimate in a *polar* medium because of correlations between the orientations of adjacent dipoles, whose effect is embodied in his "reaction field." This reaction term depends on the size of the cavity, and only by taking it equal to the mean molecular volume do his formulas reduce to the Lorentz or Clausius-Mossotti expressions in the nonpolar case.

There is apparently no easy way to decide by simple physical considerations whether the Onsager or Lorentz model is really the better. At first sight, the Onsager method seems preferable since it allows the surroundings of a molecule to adjust themselves to the latter's rotation. However, the average period of a molecule's free rotation is short compared with the relaxation time of a polar dielectric, as determined by Debye's well-known theory of dispersion at radio frequencies.⁵ If the rotations are thus so rapid that other molecules cannot follow them at all, the Lorentz model should be the truer picture.⁶ In the case of molecules of the HCl type, which have only two rotational degrees of freedom, this objection to the Onsager method may be disposed of by noting that the only contribution to the dielectric constant comes⁷ from the irrotational state $J=0$. With molecules of the H₂O type, which have three rotational degrees of freedom, and which comprise most polar molecules, all the states are effective. The largest individual contributions, to be sure, come from the states with low rotational frequencies for the dipole moment⁸ but it is not clear whether the resulting weighting of the low states is sufficient to dispose of the difficulty.

In view of this uncertainty, it is particularly interesting to compare the Onsager formula with the one obtained by the method of partition functions,—a very different procedure, which is exact as far as it goes, but in which it is feasible to compute only the first few terms in a series development in the dipole-dipole interaction. It was shown in Section 5 of l.c. that both methods

⁵ P. Debye, *Polar Molecules*, Chap. V.

⁶ I am indebted to Professor Hans Mueller for pointing out this difficulty in the Onsager model.

⁷ Cf., for instance, R. de L. Kronig, Proc. Nat. Acad. Sci. **12**, 488 (1926).

⁸ See Kronig, *ibid.* **12**, 611 (1926).

agree to the second approximation in the dipole-dipole interaction,—one order more than with the Lorentz relation. The proof was given only for permanent dipoles, but is unimpaired by inclusion of the induced polarization if the latter is represented by the usual artifice of harmonic oscillators. Namely, to the approximation in question,⁹ $f-1$ equals $-32\pi^2 N^2 \mu^4 q / 81 k^2 T^2$, and then (5) and (7) are equivalent to terms in μ^6 if $Q = 2(4\pi/3)^2$. In any case, as stressed at the very end of l.c., such agreement is secured only by using this value of Q corresponding to a continuum. A natural way of empirically modifying (7) to conform to other more real values of Q is to multiply the right side of (7) by a factor $(9/32\pi^2)Q$.

There is no doubt that the Onsager formula (7) works much better than the Gaussian one (5). According to (5), the dielectric constant can never exceed 4.7, as one sees by minimizing the denominator of (5) with $q=1$. The assumption $q=1$ is legitimate, as induced polarization is usually subordinate in polar media. Actually ϵ for H_2O is around 80, while even HCl has values of ϵ as high as 17. Furthermore Eq. (5) predicts that $d\epsilon/dT > 0$ when $T < 3\theta Q^{1/4}/4\pi$; e.g., when $T < .91\theta$ if $Q = 14.4$. In reality the dielectric constant continues to increase with decreasing temperature down to values of T far less than θ (e.g. to 273°K in H_2O , whereas $\theta = 1200^\circ$). On the other hand, Onsager shows that for suitable values of n , his formula (7) is for large ϵ nearly the same as Wyman's¹⁰ empirical relation $4\pi N\gamma/3 = (\epsilon+1)/8.5$, which fits quite well a considerable body of experimental data. This resemblance to Wyman's formula, would, however, be lost if (7) were modified as suggested above to conform to actual values of Q , and we believe that it is over-optimistic to attach much fundamental significance to quantitative fitting of the

unmodified formula (7) to experimental measurements on polar liquids. Nevertheless, (7) does appear to have the proper qualitative trend away from the Clausius-Mossotti formula. Namely, if either (5) or (7) is used, (2) ceases to be valid. Now it is well known that the Clausius-Mossotti relation (2) is not obeyed in polar liquids and solids. The difficulties are shown strikingly if we use (3), which is essentially equivalent to (2), and neglect induced polarization by taking $q=1$. Eq. (3) then predicts that the dielectric constant becomes infinite at a critical temperature θ . This behavior we shall refer to as a $4\pi/3$ catastrophe, since it arises from the term $4\pi P/3$ in the local field, without which the denominator of (3) would be simply T . Of course the dielectric constant would not really become infinite, as it is necessary to consider saturation corrections when T is below θ . The physical meaning of the $4\pi/3$ catastrophe, if it occurs, is thus that there is a critical temperature below which there is the electric analogue of ferromagnetism—i.e., saturation, hysteresis, remanence, etc. Actually, such a behavior is practically unknown, being confined largely to Rochelle salt, even if T is reduced to a small fraction of the values of θ given by (4). For example, though θ is 260° for HCl and 1200°K for H_2O , no spontaneous polarization is ever observed for these substances, even at the temperature of liquid air. According to either the Gaussian formula (5) or the Onsager expression (7), spontaneous electric polarization is impossible. The case of Rochelle salt must be regarded as special, since this is an anisotropic body for which the factor Φ in the customary local field $E + \Phi P$ can be much larger than $4\pi/3$ along certain directions. In fact, inspection of Fowler's model¹¹ for Rochelle salt shows that it is quite possible to construct values of Φ considerably greater even than the minimum value¹² 8.2 which is required for spontaneous polarization with a Gaussian calculation and which is probably an over-estimate. It is thus doubtful whether a $4\pi/3$ catastrophe should occur in an isotropic medium.

One thing is certain, and that is that the energy of a collection of dipoles is not rigorously a minimum when they

⁹ This value of $f-1$ follows on substituting in (7a) the approximate value (3) of ϵ and disregarding cubes of μ^2 or α . This substitution is legitimate, since $f-1$ need only be computed to the approximation μ^4 in evaluating (7) to μ^6 . In comparing (5) and (7), the right side of (5) may be considered equivalent to $3q\theta[1 - (9Q\theta^2/16\pi^2 T^2)]/(T - q\theta)$ since (5) is only rigorous to θ^3 or μ^6 . Accuracy to μ^6 represents a second approximation in the dipole-dipole interaction, since even without this coupling the susceptibility involves μ^2 , and since the dipole-dipole potential is proportional to the product of two elementary moments, i.e., to μ^2 .

¹⁰ J. Wyman, Jr., J. Am. Chem. Soc. **58**, 1482 (1936).

¹¹ R. H. Fowler, Proc. Roy. Soc. **149A**, 1 (1935).

¹² Cf. remarks following (57) of l.c.

are all parallel. The fact that the total resultant moment P is not a constant of the motion when the interaction between the elementary dipoles is of the true dipole-dipole rather than exchange type immediately shows that mutually parallel orientation cannot give an exact extremum of energy. Instead the wave function for the deepest state will be a linear combination compounded from various possible eigenvalues of P . Of course, this argument would not preclude the possibility that large values of P are dominant in the linear combination, and then one would have a quasi-ferromagnetic condition. With a simple cubic arrangement it seems much more probable that actually the low values of P are dominant. Indeed an elementary classical calculation shows that lower values of the energy than for parallel alignment are obtained when the dipoles are arranged in parallel strings, such that along a string the dipoles all point the same way, but with the directions of the dipoles opposite in adjacent strings; thus: $\rightleftharpoons \rightleftharpoons \rightleftharpoons$. An arrangement of this type gives an energy $-2.7N^2\mu^2$ for a simple cubic lattice, as compared with $-\frac{1}{2}(4\pi/3)N^2\mu^2 = -2.1N^2\mu^2$ for parallel alignment along a long slab (the most favorable case). With the body-centered and face-centered lattices, however, the coefficient -2.7 is replaced by 0 and $+1.9$, respectively, so that the parallel configuration gives deeper energy than alternating strings.¹³ This result is, of course, inconclusive because there are many other conceivable nonferromagnetic arrangements besides alternating strings. Still, it is perhaps significant that in the alum salts in which Kürti and Simon report some evidence of ferromagnetism due to dipole-dipole coupling (cf. end of Section 3) the paramagnetic ions are spaced on a face-centered rather than simple cubic lattice. On the other hand, solid hydrogen chloride, which fails to exhibit the electric analogue of ferromagnetism, also has a face-centered lattice. With Fowler's model of Rochelle salt, which is anisotropic and which has the distance between strings considerably larger than the separation of atoms along a string, it seems reasonably clear that much the lowest energy is obtained when the dipoles are all practically parallel. This situation, of course, accords with the known spontaneous polarization of Rochelle salt exhibited along certain directions.

In any event, the calculation of the states of low energy is a far more complicated affair with our dipole-dipole forces than for ordinary exchange or ferromagnetic coupling, where the mutual energy of two dipoles does not depend on how they are oriented relative to their connecting line. Approximation by means of the Lorentz formula, however, does not bring out at all the essential differences between the two cases, as the Lorentz local field differs from the Weiss-Heisenberg one only in the proportionality factor. If there are really any remanence phenomena due to dipole-dipole coupling, they may well be quite different in character than for ordinary ferromagnetic media.

¹³ These coefficients have been computed for me by Dr. M. H. Hebb. The zero value for the body-centered lattice is also noted by Fröhlich, *Proc. Roy. Soc.* **158A**, 97 (1937). In the face-centered case, if the strings are along the 110 rather than 100 axis, the coefficient is reduced somewhat from 1.9, but still remains greater than -2.1 .

3. RELATION TO THE FOWLER-DEBYE THEORY

The preceding considerations have an interesting bearing on the theory of the dielectric constant of polar liquids and solids developed independently by Fowler¹¹ and by Debye.¹⁴ To explain the absence of spontaneous electric polarization, they postulate some mechanism in the solids or liquids which can "congeal" the dipoles, so that they are not free to orient, and the susceptibility has in consequence a value much lower than that given by the usual Langevin-Debye formula. It is to be understood throughout that the word "congealing," as we use it, relates to the suppression of free rotation, and does not necessarily have anything to do with the passage from the liquid to the solid state, since the melting point may be quite different from the critical temperature at which free rotation is acquired. In the case of Rochelle salt, which is highly anisotropic and is unusual in exhibiting the electric analogue of ferromagnetism, the hindered rotation suggested by Fowler seems necessary to explain why its spontaneous polarization disappears when the temperature is reduced sufficiently. A different situation, however, is presented by isotropic materials. We have seen that it is very questionable whether an isotropic dielectric body can ever acquire spontaneous polarization simply in virtue of dipole-dipole coupling. If the $4\pi/3$ catastrophe does not exist, it is clearly not necessary to introduce the hypothesis of hindered rotation to explain its non-occurrence.

Instructive evidence is presented by the hydrogen halides, which appears to have been generally overlooked, and which suggests that hindered rotation is not required to prevent spontaneous electric polarization. On the basis of (4) one calculates that the Curie point θ for HCl is about 260°K for HCl, and about 120° for HBr. The absence of saturation can scarcely be blamed on any "congealing" of the dipoles, since a $4\pi/3$ catastrophe is avoided with the Clausius-Mossotti formula only if θ is less than the congealing temperature and since it is generally regarded as known from other evidence (specific heats, etc.) that the transition temperatures at

¹⁴ P. Debye, *Physik. Zeits.* **36**, 100 (1935).

which free rotation is suppressed are,¹⁵ respectively, 100° and 90° for HCl and HBr. At these temperatures there are large discontinuities in the dielectric constant, which have been correlated by Pauling,¹⁵ and others with the cessation of free rotation. One cannot invoke the congealing of the dipoles to explain the absence of spontaneous polarization over the interval 100 – 260° in HCl or 90 – 120° in HBr, and at the same time suppose that sudden loss of free rotation explains anomalies at 100° and 90° respectively. It appears probable that the latter is the correct use. Therefore it seems natural to assume that the absence of spontaneous polarization is to be attributed simply to the inadequacy of the ordinary Lorentz local field, which does not take sufficient cognizance of the fluctuations in the interatomic forces due to variable alignment of the dipoles surrounding a given dipole. Such fluctuations are implicitly involved in the higher approximations in the method of partition functions, while the Onsager model allows for them through his "reaction field," as well as in the main ("direct") part of the field through the redistribution of lines of force due to the existence of the cavity (cf. Fig. 1 of l.c.). Now, as already stated, neither Eq. (5) based on a Gaussian extrapolation of a statistical calculation nor Eq. (7) derived from the Onsager theory ever allows spontaneous polarization. Very likely (5) goes too far, as any Gaussian calculation tends to over-estimate the influence of fluctuations in suppressing saturation phenomena. However, to explain the non-occurrence of a $4\pi/3$ catastrophe in HCl, it is only necessary to suppose that the fluctuation effects make the critical temperature for spontaneous polarization very much lower than that given by (3).¹⁶ In the case of the Heisenberg theory of ferromagnetism, it would be difficult to believe

that the Curie temperature given by a nonspreading assumption, comparable to (4) is in error by a factor so large as $2.6 = 260/100^\circ$, as we would have it in the case of HCl. However, it was shown in Section 5 of l.c. that the fluctuation effects are much more important for dipole-dipole than exchange coupling, and the resulting modification of the Curie temperature correspondingly larger.

The situation in H_2O , CH_2O_2 , etc. is less clear than in the hydrogen halides. Large discontinuities in the dielectric constant in H_2O occur at the melting point, unlike the cases of HCl, HBr. If consequently the melting point is accepted as the critical congealing temperature for the free rotation, one has again the difficulty that this temperature is much less than the critical temperature given by (4), so that hindered rotation would not prevent the $4\pi/3$ catastrophe. Hence Fowler assumes somewhat artificially that the dipoles are partially congealed even at the boiling point, enough to prevent spontaneous polarization, and that there is additional congealing at the melting point. The assumption of two real critical congealing temperatures is obviously not attractive. However, the interesting question arises as to whether there may not be some tautology between his model and our fluctuation effects, or in other words how much of the apparent congealing envisaged in the F-D theory may be in part a manifestation of the dipole-dipole potential, rather than true hindered rotation of the Pauling type due presumably to short range forces, e.g., higher order poles, not covered by our calculations with dipole-dipole coupling.

We have based all our discussion so far on the part of l.c. corresponding to atoms which are free except for dipole-dipole coupling. One therefore inquires whether the short-range forces might not be represented by superposing a crystalline field, as in Section 6 of l.c. Unfortunately a simple calculation shows that in classical theory crystalline fields which have a center of symmetry do not modify the dielectric constant if they are distributed at random.¹⁷ In quantum mechanics

¹⁵ L. Pauling, *Phys. Rev.* **36**, 430 (1930); cf. also the related experimental work on the hydrogen halides by R. M. Cone, G. H. Denison and J. D. Kemp, *J. Amer. Chem. Soc.* **53**, 1278 (1931) and by C. P. Smyth and C. S. Hitchcock, *ibid.* **55**, 1830 (1933).

¹⁶ If, as suggested after (7), the right side of (7) is reduced by a factor $9Q/32\pi^2$, the resulting critical Curie temperature is $T_c = \theta(q - 9Q/32\pi^2)$. If then one uses the value 14.4 of Q appropriate to a face-centered lattice, such as is found in solid HCl, the resulting value of T_c is 106° (taking $q = 1$). The difficulty regarding spontaneous polarization thus reappears, since other evidence indicates that free rotation is destroyed only below 100° . Quantitative accuracy, however, is not claimed for our proposed modification of (7).

¹⁷ See, for instance, H. Mueller, *Phys. Rev.* **50**, 547 (1936). In this very interesting paper, Mueller shows that even symmetric potentials can influence the dielectric constant in case the Lorentz factor Φ depends on direction

this result is not rigorously true, but at ordinary temperatures the spacing of rotational energy levels is sufficiently close that the classical procedure represents a good approximation. If one utilizes fields without a center of symmetry, one has a dissymmetry of a type which is suggestive of dipole-dipole coupling, especially since Fowler has his unsymmetrical fields fade out when the polarization of the medium diminishes (his "co-operative" effect).

Saturation. What has previously seemed one of the most attractive arguments in favor of the Debye-Fowler theory is furnished by Debye's calculation¹⁸ of saturation under the hypothesis of hindered rotation. Namely, in very strong applied fields the dielectric constant ceases to be independent of field strength. At the voltage gradients obtainable experimentally, the deviation $\Delta\epsilon$ from the ordinary value ϵ_0 for weak fields is a quadratic function of the field strength, so that

$$D/E = 1 + 4\pi P/E = \epsilon_0 + \Delta\epsilon = \epsilon_0 + aE^2. \quad (8)$$

If it is assumed that dipole-dipole interaction can be represented by proper choice of a local field E_{loc} and if induced polarization is neglected then the polarization per unit volume is given by

$$P = N \left(\frac{\mu^2}{3kT} E_{loc} - \frac{\mu^4}{45k^3T^3} E_{loc}^3 \right). \quad (9)$$

Eq. (9) is merely the conventional Langevin formula inclusive of the terms corresponding to incipient saturation. If the usual Lorentz local field is employed, the resulting value of the saturation correction is

$$\Delta\epsilon = -4\pi \left(\frac{1}{3}\epsilon_0 + \frac{2}{3} \right)^4 (N\mu^4/45k^3T^3) E^2, \quad (10)$$

as is seen setting $E_{loc} = E + 4\pi P/3$ in (9), substituting the value (8) of P/E and solving for a with neglect of fourth powers of E . At a field of 100,000 volts/cm., the value of $\Delta\epsilon/\epsilon$ calculated from (10)

and so differs from $4\pi/3$. This effect may well be important in liquids with marked cybotatic structure, where the molecules tend to arrange themselves in locally anisotropic regions. Another possibility is that if in a cybotatic group the molecules have the alternating string arrangement mentioned at the end of Section 2, an unsymmetrical potential of the Fowler-Debye type may be a rough way of allowing for the increase in energy attendant to reversing a dipole against the ordinary dipole-dipole forces. These considerations obviously have no bearing in the case of solid HCl above 100°, which has a face-centered cubic lattice and so is highly isotropic.

¹⁸ P. Debye, *Physik. Zeits.* **36**, 193 (1935).

for water (where $\epsilon = 80$, $\mu = 1.84 \times 10^{-18}$) is -3.87 , whereas Malsch's¹⁹ experimental value is only -1.1×10^{-3} . To account for this discrepancy in order of magnitude, Debye introduces hindered rotation. As already emphasized, it is necessary to assume that the crystalline field is unidirectional rather than with a center of symmetry. Debye then calculates the factors R and R^* by which the first and second terms of (9) are reduced. We omit repeating the explicit formulas here. Using in R^* the value of the hindering field obtained from R , he calculates a value of $\Delta\epsilon/\epsilon$ which agrees almost perfectly with the experimental determination by Malsch.

In our opinion, however, the agreement thus achieved ceases to be impressive, or an argument for assuming hindered rotation (unless construed as tautological with dipole-dipole coupling) when it is remembered that the Lorentz field is not rigorous. If instead we use in (9) the Onsager field, *viz.*

$$E_{loc} = [3D/(2D+E)]E, \quad (11)$$

then in the same way as (10) was previously obtained, we find that with free rotation

$$\Delta\epsilon = -4\pi \left(\frac{N\mu^4}{45k^3T^3} \right) \left[\frac{27\epsilon_0^4}{(2\epsilon_0^2+1)(2\epsilon_0+1)^2} \right] E^2. \quad (12)$$

Only the "direct" part of the local field is included in (11), as the reaction portion has no effect on molecular orientation. The value of $\Delta\epsilon/\epsilon$ calculated from (12) at 100,000 volts per cm is -2.4×10^{-5} . The fact that this is considerably lower in magnitude than Malsch's experimental value -1.1×10^{-3} need not give concern. The point is that the preposterously high value of $\Delta\epsilon/\epsilon$ given by the Lorentz field is entirely avoided, and it is not necessary to introduce hindered rotation to suppress excessive saturation curvature. The absence of quantitative agreement is not surprising, as Onsager himself states formula (11) "is not in general applicable to strong fields, i.e., saturation; because its derivation involves the assumption of an isotropic environment." This observation, however, applies mainly to nearly complete rather than to incipient saturation such as we are studying. We believe that the Onsager model still has at least

¹⁹ J. Malsch, *Physik. Zeits.* **30**, 837 (1929).

qualitative meaning since its vital feature, that at high polarizations the directive part of the local field is smaller than the Lorentz expression, is very relevant for all calculations on saturation. The fact that $\Delta\epsilon/\epsilon$ is larger experimentally than the value given by (12) is in line with our observation that the Onsager model demands a higher value of the quantity Q defined in (6) than corresponds to actual discrete arrangements and so perhaps overaccentuates deviations from the formulas obtained by the conventional Lorentz procedure.

Bearing of recent magnetic experiments. We must mention that new experiments by Kürti, Lainé, and Simon²⁰ indicate that paramagnetic salts acquire some traces of ferromagnetism at very low temperatures, namely, a feeble remanence and hysteresis. The interesting question arises as to whether this behavior is caused by (a) spontaneous polarization due to dipole-dipole coupling, qualitatively of the type given by the Lorentz local field, (b) exchange forces, or (c) special factors somehow connected with the presence of very low temperatures.

(a) If (a) is the correct explanation, it is very hard to understand why the remanence occurs in paramagnetic but not in dielectric materials. The calculations are, to be sure, not quite the same in the two cases because of the noncommutative terms in the former. However, Eq. (55) of I.c. shows that these terms increase the apparent value of Q , and so work in the wrong direction, tending to suppress saturation in the magnetic rather than electric case. Instead, if hypothesis (a) is accepted, to explain the non-occurrence of spontaneous polarization in dielectrics, it would presumably be necessary to suppose that there is some type of cooperative effect peculiar to the latter and probably somehow associated with the finite length of the dipoles in the electric case. This would be essentially a reversion to the Fowler-Debye hindered rotation, with the attendant difficulties in understanding the behavior of HCl at 100°K.

A crucial experiment which seems to decide against (a) is obtained by investigating the dependence on the shape of the test body. According to (a) any incipient ferromagnetic behavior should be present only in very long specimens. Professor Simon informs the writer that actually the remanence and hysteresis are found even for spherical bodies, to be sure with greatly diminished area in the hysteresis loop, but at a critical entropy and hence presumably at a critical temperature which does not differ greatly from that with long samples. If (a) were correct, the Curie point should vary tremendously with shape and vanish for spheres.

(b) It is usually assumed that in paramagnetic salts, in distinction from true ferromagnetic media, the exchange forces can be disregarded because of the large separation between paramagnetic ions. However, Kramers²¹ has

²⁰ Kürti, Lainé, and Simon, *Comptes rendus*, **204**, 675, 754 (1937).

²¹ H. A. Kramers, *Physica* **1**, 182 (1933).

pointed out that owing to the intervention of the excited states of intermediate, normally diamagnetic atoms, the dependence of the exchange forces upon distance may be less drastic than in the usual exponential type. Hence they may not be negligible. The desired approximate independence of the Curie point of shape can be obtained if the exchange forces are large compared to the dipole-dipole, but then there is the difficulty that the Curie point would be too high, and the deviations from Curie's law too great at helium temperatures. If exchange forces are important only in certain small domains where the atoms are abnormally close together because of crystalline imperfections, this difficulty may disappear. Then, however, it is impossible to understand the great fall in entropy at the remanence temperatures, which indicates that practically all rather than a few atoms are involved in the anomaly, unless one makes the highly improbable assumption that it is a sheer accident that the maximum in specific heat and the acquisition of remanence occur at the same temperature. So all forms of (b) seem to encounter difficulties.

(c) If the remanence and hysteresis are somehow characteristically connected with the very low temperatures found in the magnetic cooling experiments, there is obviously no contradiction with the behavior of dielectrics. Heitler and Teller²² have shown that there is probably thermodynamic equilibrium between the elementary magnets, but not between them and the lattice vibrations. In dielectrics, on the other hand, we are concerned with much higher temperatures, where the lattice vibrations, as well as the dipole-dipole interaction, can convey energy from one dipole to another. Conceivably certain exceptional dipoles tend to remain "stuck" parallel to the field except as disturbed by vibrational effects, and in this way there might be hysteresis only in the magnetic case. This mechanism, however, yields no insight into the rather large increase in susceptibility concomitant to the appearance of remanence. However, it must be remarked that this increase is nothing like as large as in true ferromagnetic media.

All told, it seems probable that the remanence phenomena observed by Kürti, Lainé, and Simon are not a true $4\pi/3$ catastrophe, and cannot necessarily be construed as evidence that hindered rotation is required to prevent the occurrence of the latter. In any event, their experiments present an interesting and difficult problem for the theoretical physicist, and additional data are greatly to be desired.

4. NONPOLAR LIQUIDS OR SOLIDS

Much of the evidence for the C-M formula is from gases at high pressures, where $\epsilon - 1$ is small compared to unity, so that to a sufficient approximation

$$\frac{M(\epsilon - 1)}{\rho(\epsilon + 2)} = \frac{M}{3\rho}(\epsilon - 1)\left[1 - \frac{1}{3}(\epsilon - 1)\right]. \quad (13)$$

²² W. Heitler and E. Teller, *Proc. Roy. Soc.* **155A**, 629 (1936).

However, the C-M expression works remarkably well empirically even for nonpolar liquids. Particularly striking examples are furnished by N_2 and O_2 . The C-M ratio; i.e., the left side of (13) has the magnitude 3.869 in O_2 gas, and an almost identical value 3.878 in the liquid, despite the fact that the density differs by a factor over a thousand.²³ The corresponding quantities for N_2 are 4.395 and 4.396. Also there is a mass of experimental evidence that even in polar materials the Lorentz-Lorenz ratio, which is similar except that ϵ is replaced by the square of the optical index of refraction, has often nearly equal values in the gaseous and liquid states. We do not treat explicitly the subject of optical rather than static polarizability, but since the optical refractivity arises entirely from induced polarizability, and is nearly equal to the latter's contribution to the dielectric constant, all the difficulties and other considerations which we raise in connection with the Clausius-Mossotti formula in nonpolar materials also apply to the Lorentz-Lorenz expression even in polar media.

At first thought one might attribute the success of the C-M formula for induced polarization to the fact that only one electronic state has an appreciable Boltzmann factor for each atom or molecule. If the unit of structure is molecular rather than atomic, the rotational and vibrational structure of the ground state may be congealed out by the crystalline field in liquids or solids, and anyway is of subordinate importance for induced rather than permanent polarization. Hence one needs to consider only one state for the "crystal" as a whole (i.e., entire liquid or solid) and the need of developing the partition function as a series in $1/kT$ can be avoided by proper choice of origin. However, this simplification alone does not give the C-M formula (2) since actually to include the dipole-dipole coupling rigorously, one must determine accurately the lowest eigenvalue of the whole liquid or solid, obviously a hopeless task. (Mathematically this difficulty is expressed in the fact that in e.g., the second order of approximation, the last term in Eq. (72) of l.c. persists in contributing to the polarization even if we can omit all portions of $kT \log Z$ with powers of T in the

denominator.) The local field method is not rigorous, because even without dipole rotation the moment of an atom oscillates due to the motion of the electrons in their orbits, and so the square of the mean field which it exerts is not equal to the mean square. All that one can say in general about the induced polarization is that the Clausius-Mossotti formula should be valid to a degree of approximation comparable to neglecting the difference between the left and right sides of (13). This accuracy, however, is not sufficient to depict the experimental facts, as in e.g., liquid O_2 the left side of (13) has the value 3.878, and the right side 3.774, whereas the experimental deviations from (2) are of the order 0.01 rather than 0.1. It is therefore imperative to find some model which will yield the C-M formula (2) rigorously. We show below in fine print that (2) is obtained to all orders of approximation if each atom is regarded as an isotropic harmonic oscillator.²⁴ However, such a model cannot be regarded as bearing much resemblance to a real Rutherford atom. It should be possible to find the simplifications in the rigorous general perturbation formulas which make them furnish answers similar to those for the harmonic oscillator. In this connection, the Onsager model, at least in its original form, sheds no additional light, since it implicitly uses the harmonic model, and so yields the C-M formula in the case of induced polarization. We have in mind rather the work of Serber.²⁵ He showed that the reason why the conventional formulas based on harmonic oscillators work empirically so well in the Kerr effect and in the depolarization of light is that the general quantum-mechanical atom also yields the same formulas if one makes the "centroid" assumption that all the important absorption frequencies of the atom are nearly equal. By

²⁴ Incidentally the rigorous validity of the Clausius-Mossotti formula for isotropic harmonic oscillators shows that Lorentz's calculation of the local field was entirely correct for the model which he used. The Onsager procedure can represent an improvement only for the part of the polarization arising from permanent dipoles, which Lorentz did not really have in mind. Our doubts as to the C-M formula for systems other than harmonic oscillators are not to be confused with the objections raised by Kronig and Groenewold (Proc. Amst. Acad. 35, 974, 1932) and by Darwin (Proc. Roy. Soc. 146A, 17, 151A, 572, 1934-5). These authors were concerned with conductors, while we are dealing with insulators. Cf. R. H. Fowler, *Statistical Mechanics*, second edition, p. 437ff.

²⁵ R. Serber, Phys. Rev. 43, 1003 (1933).

²³ For references, see Zahn and Miles, Phys. Rev. 32, 502 (1928).

analogy with his work one is thus led to investigate the hypotheses which will make the C-M formula valid at least in the second approximation in the general treatment in Section 6 of l.c. Eq. (82) of l.c. shows that this requires that $2\alpha^{(2)}kT = Q\chi_0^3$. However, detailed examination, of which we omit the details, shows that this condition is not met merely in virtue of a centroid assumption, but requires in addition that the excited states (involved through matrix multiplication contained in perturbation formulas rather than through appreciable Boltzmann factors) have the same polarizability as the ground state, and that the energy states be evenly spaced. Only the harmonic oscillator possesses these characteristics. It must hence be regarded as an unanswered question why the C-M formula works as well as it does in nonpolar liquids. The best that one can do is to say that the harmonic model surely comes closer to representing induced polarization than that due to permanent dipoles, and so the C-M formula should apply more closely to nonpolar than polar liquids, but this argument gives no insight into why it should apply so exactly to the former.

Derivation of the Clausius-Mossotti formula with the harmonic oscillator model. Let the normal coordinates of a given atom j be $\xi_{1j} \cdots \xi_{fj}$ and let $p_{1j} \cdots p_{fj}$ be the corresponding momenta. The z component, for instance, of the electric moment of any given atom will be a linear function $\sum_i d_{ij} \xi_{ij}$ of its normal coordinates. The Hamiltonian function for the totality of atoms in the solid is

$$\mathcal{H} = \sum_{ij} \left\{ \frac{1}{2} a_{ij} p_{ij}^2 + \frac{1}{2} b_{ij} \xi_{ij}^2 - E_0 d_{ij} \xi_{ij} \right\} + \sum_{ij, i'j'} C_{ij, i'j'} \xi_{ij} \xi_{i'j'}. \quad (14)$$

Here the first term is the kinetic energy, the second the internal potential energy of the various atoms, the third the electric potential due to the applied electric field E_0 , which we have supposed directed along the z axis, and the fourth the dipole-dipole energy. Note that E_0 is not the same as E , since E_0 is the field before insertion of the specimen. The explicit value of $C_{ij, i'j'}$ is (cf. Eq. (5) of l.c.)

$$C_{ij, i'j'} = C_{i'j', ij} = \sum_{q, q' = x, y, z} [\delta_{q, q'} - 3 \cos(q, r_{ij}) \cos(q', r_{i'j'})] d_{ij}^q d_{i'j'}^{q'} \quad (15)$$

The linear terms in ξ_{ij} may be eliminated from (15) by shifting the origins of the ξ_{ij} to new values ξ_{ij}^0 which are linear in E_0 and are the roots of the simultaneous linear equations

$$b_{ij} \xi_{ij}^0 + 2 \sum_{i'j'} C_{ij, i'j'} \xi_{i'j'}^0 = E_0 d_{ij}^z. \quad (16)$$

The partition function is then

$$Z = \text{spur} \exp(-\mathcal{H}/kT) = Z^0 \exp \Gamma E_0^2, \quad (17)$$

where Z^0 denotes the partition function for $E_0 = 0$ and

where

$$\Gamma E_0^2 = \frac{1}{2} \sum_{ij} b_{ij} \xi_{ij}^0{}^2 + \sum_{ij, i'j'} C_{ij, i'j'} \xi_{ij}^0 \xi_{i'j'}^0.$$

The arguments of Z^0 are not the original normal coordinates $\xi_{11} \cdots \xi_{fN}$ and their corresponding momenta, appropriate to free atoms not exposed to external fields. Instead they are new coordinates $\xi_{11} - \xi_{11}^0, \dots, \xi_{fN} - \xi_{fN}^0$ which include the shift in origin necessary to eliminate the linear terms from (14). The conjugate momenta are unaffected by this shift. However, the functional form of Z^0 is the same as before application of E_0 and so its numerical value does not depend on E_0 ; Thus the moment is

$$P = \frac{\partial}{\partial E_0} \log Z / \partial E_0 = 2 \Gamma E_0 = \sum_{ij} d_{ij} \xi_{ij}^0, \quad (18)$$

the final form being obtained by using (16). Now $\sum_j d_{ij} \xi_{ij}^0$ is simply the moment possessed by atom j calculated as a problem in pure electrostatics by finding the equilibrium value ξ^0 of each ξ under the simultaneous influence of three types of forces (I) the internal potential energy, (II) the external field, (III) the dipole-dipole interaction. For such a problem the dipole-dipole coupling is equivalent to a suitable local field, e.g., $E + 4\pi P/3$ if there is cubic symmetry and if the atoms are isotropic.²⁶ In fact, this is precisely the way in which one obtains the conventional formulas for the local field. Our derivation differs only that it is by statistical mechanics, inclusive of momentum terms, rather than by electrostatics.

It is perhaps at first sight rather surprising that the result still holds even with our kinetic method, for when the particles oscillate about their equilibrium positions, the mean square field is not the same as the square of the mean field, and so conceivably fluctuation effects might enter. The reason that the latter do not really spoil things is that even with the dipole-dipole coupling, the Hamiltonian function is still a quadratic function of the ξ^0 's. Consequently the method of normal coordinates can still be applied provided we take the whole crystal rather than a single atom as the structural unit, and any system representable by normal coordinates always yields (2).

The preceding calculation is perfectly valid in quantum mechanics, where the ξ 's and p 's are to be regarded as matrices. The ξ^0 's are, on the other hand, mere constants ("c numbers," in Dirac's terminology) and so Γ commutes with the rest of the Hamiltonian function, and there are no difficult questions of ordering, etc. We have, in fact, regarded our preceding calculation as quantum mechanical by labeling in (17) the partition function as a spur. Classical language could, of course, be used instead, and then the spur would be replaced by an integral over phase space.

If the oscillators are anisotropic and are not all oriented in the same way, they will vary among themselves both as regards polarizability relative to a given fixed direction and as regards the local field to which they are subject. The displacement from equilibrium position is the product of the polarizability and effective field; and the mean product, which enters in the formula for the dielectric constant, is

²⁶ For proof that for cubic symmetry the local field with discrete spacings of atoms is sensibly the same as with the continuum assumed by Lorentz, see Ewald, *Ann. d. Physik* **49**, 1 (1916).

not the same as the product of the means, because of the variations mentioned in the preceding sentence. In other words the approximation (78) of l.c. may not be satisfied. In an interesting paper, Kirkwood²⁷ has considered the deviations from the C-M formula due to this cause, which he calls a rotational fluctuation effect,—not to be confused with the translational fluctuations discussed in the next section. We prefer to call these deviations a disordering effect, as they appear in the purely electrostatic approximation, which is the basis of Kirkwood's treatment. Stated in other words, they arise when the classical cavities are non-spherical and oriented at random. It is not clear whether the disordering effect or the substitution of a real atom for the harmonic model causes the larger deviations from the C-M formula. Slight departures from this formula are observed experimentally in a few cases in nonpolar liquids, e.g., pentane.²⁸

5. POLAR GASES—THE TRANSLATIONAL FLUCTUATION EFFECT

The difficulty of poor convergence of the perturbation theory can be avoided by employing gases at high pressures, as then the density is adequate to make the dipole-dipole interaction appreciable, but at the same time sufficiently low to make the higher approximations negligible. It is well known that the Clausius-Mossotti formula is confirmed by a variety of measurements on condensed gases, and is much more successful than the Dale-Gladstone law $(n-1)/\rho = \text{const.}$, which represents a very crude approximation comparable to complete neglect of the second right-hand member of (13). Nevertheless there is definite evidence that if we write

$$\frac{\epsilon-1}{\epsilon+2}V = P_0 \left[1 + \lambda \frac{P_0}{V} + \omega \left(\frac{P_0}{V} \right)^2 + \cdots \right], \quad (19)$$

where P_0 is the "molar polarization" $4\pi L\gamma/3$ (cf. Eq. (2)) and V is the molar volume, the coefficient λ of P/V is not zero as the Clausius-Mossotti formula would demand. Keyes and Kirkwood have shown that the nonvanishing λ arises from what they call a "translational fluctuation effect."²⁹ The theory developed in l.c. might suggest at first sight that $\lambda=0$ since the deviations from the C-M formula there appeared in the second rather than first approximation in the density. However, this conclusion was on the

basis of a regular spacing of atoms, whereas in a gas the atoms continually approach or recede from each other, so that the mean inverse sixth power of the distance of separation is not at all the same as the square of the mean of the inverse cube. Consequently part of what would be a term in V^{-2} , were there regular spacing, is replaced dimensionally by $V^{-1}a^{-3}$, where a is the distance of closest approach of two molecules. The coefficient λ was calculated by Kirkwood for a model consisting of harmonic oscillators or their equivalent. His computations thus apply at most only to nonpolar materials, and it therefore seems advisable to calculate λ for a more general model consisting of molecules having both a permanent dipole moment of magnitude μ and an induced polarization represented by the usual artifice of isotropic harmonic oscillators, whose coefficient of polarizability will be denoted by α . Explicit calculation, of which we give the details in fine print below, shows that

$$\begin{aligned} \lambda P_0 = & (8\pi L\alpha^2/9a^3)(3+2y) \\ & + (4\pi L\alpha^3/225a^6)(15+10y+y^2)^2(3+y)^{-1} \\ & + (4\pi L\alpha^4/225a^9)(15+10y+y^2) \\ & \times (60+60y+8y^2)(3+y)^{-1} + \cdots, \quad (20) \end{aligned}$$

with $y = \mu^2/\alpha kT$. For the nonpolar case $y=0$, Eq. (20) reduces to Kirkwood's expression if we neglect the correction factor $1+(4/3bT)$ which he includes to allow for the van der Waals' attractive forces, and if we retain terms of only the first order in $1/a^3$. In our opinion, his van der Waals' correction is extraneous, as the dipole-dipole attraction is already included to yield (20) as it stands (specifically, via the exponents in the f_{ij} in our later Eq. (24)). Hence it is redundantly counting things twice to include in addition an attractive potential of the inverse sixth power type due to polarization. The deficiencies of the harmonic oscillator model, are, however, so great that it is rather meaningless to argue profoundly over this question. Kirkwood was entirely justified in retaining only terms in $1/a^3$, since in the nonpolar case the higher order members in $1/a^5$, $1/a^9$, etc., are usually quite unimportant. With polar molecules, however, the influence of these higher terms cannot be neglected, although it does seem allowable to neglect $1/a^{12}$ and beyond,

²⁷ J. G. Kirkwood *J. Chem. Phys.* **4**, 592 (1936).

²⁸ W. E. Danforth, *Phys. Rev.* **38**, 1224 (1931).

²⁹ F. G. Keyes and J. G. Kirkwood, *Phys. Rev.* **37**, 202 (1931); a numerical error in this paper is noted by Kirkwood in footnote 6 of reference 27.

at least in ammonia. It is interesting to note that the permanent polarity alone makes no contribution in the first approximation $1/a^3$ since the first member of (20) vanishes when $\alpha=0$, $\gamma\alpha=\mu^2/kT$. Instead, in the polar case, most of the contribution to λ comes from cross terms between the induced and permanent polarization. This situation explains why excessively large values of λ are obtained if one naively attempts to apply Kirkwood's nonpolar formula to the polar case simply by replacing in Kirkwood's formula the induced polarizability by the complete polarizability $\gamma=\alpha+\mu^2/3kT$. As noted by Keyes and Oncley,³⁰ such a procedure would yield $\lambda=2$ in NH_3 . This is the sole polar gas for which measurements of λ are available, and the observed value of λ is only 0.3, of a different order of magnitude. Keyes and Oncley thus suggest empirically that somehow the induced is relatively more effective than the permanent polarization in contributing to λ , and their conjecture is nicely borne out by the theoretical calculations. The value of λ which (20) yields for NH_3 is 0.4. The discrepancy is no greater than

the experimental error. Existing measurements over a temperature range are not sufficiently accurate to test the theoretical temperature dependence. Accurate agreement between theory and experiment is not to be expected, because of experimental error and especially because induced polarization cannot be adequately represented by harmonic oscillators, as stressed in the preceding section. The latter fact possibly explains why the observed values of λ are usually larger than the computed ones in nonpolar gases. The opposite trend, however, is found in the polar material NH_3 . Another source of error is that the repulsive potential is not actually of the infinitely sudden type demanded by our hard sphere model.

Existing experimental data are inadequate to yield the second coefficient ω in (19). So we shall not assay the theoretical calculation of ω . We may, however, note that the leading term in a development of ω in powers of $1/a^3$ has the value $-15/16$, so that $\omega = -(15/16) + O(1/a^3) + \dots$. This result was established by Kirkwood for the harmonic oscillator model, but can be shown to hold for the general molecule.^{31, 32}

Proof of Eq. (20). For our purposes, it will be an adequate approximation to use classical mechanics.³³ The Hamiltonian function is

$$\mathcal{H} = \frac{1}{2} \sum_i b_i \mathbf{r}_i^2 - E_0 \sum_i m_i z_i + \sum_{i>j} w_{ij}, \quad (21)$$

where

$$\mathbf{m}_i = \mathbf{p}_i + e_i \mathbf{r}_i, \quad w_{ij} = r_{ij}^{-3} [\mathbf{m}_i \cdot \mathbf{m}_j - 3r_{ij}^{-2} (\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})]. \quad (22)$$

The first term in (21) is the harmonic binding energy, supposed isotropic. The harmonic displacement vector \mathbf{r}_i is not to be confused with the separation \mathbf{r}_{ij} between the centers of atoms i and j . The total moment \mathbf{m}_i of a typical atom i arises from a permanent portion \mathbf{p}_i and an induced contribution $e_i \mathbf{r}_i$, where e_i is the effective charge associated with the molecular oscillation. The partition function is

$$Z = \int \cdots \int \exp(-\mathcal{H}/kT) dv_1 \cdots dv_L d\tau_1 \cdots d\tau_L,$$

where $dv_i = r_i^2 \sin \theta_i \sin \Theta_i dr_i d\theta_i d\varphi_i d\Theta_i d\Phi_i$ and where Θ , Φ , and θ , φ are the polar coordinates specifying the orientation of the vectors \mathbf{p}_i and \mathbf{r}_i respectively while $d\tau_i$ is the volume element in which the center of atom i is located. We suppose that there is a gram mole of material, so that there are L molecules in all. It has not been necessary to include either the oscillational or rotational kinetic energy, as this contributes to Z a factor independent of E_0 which is of no importance for our purposes. (The integration over the rotational momenta does, however, contribute a factor $\sin \Theta_i$ in the volume

³⁰ F. G. Keyes and J. L. Oncley, Chem. Rev. **19**, 195 (1936): based on experimental work by Keyes and Kirkwood, Phys. Rev. **36**, 1570 (1930) and by Uhlig, Kirkwood, and Keyes, J. Chem. Phys. **1**, 155 (1933).

³¹ The term in question is shown by Kirkwood to arise from the excluded part of a sum of the type $\sum_{(k \neq i)} r_{ij}^{-3} r_{ik}^{-3}$. This part gave rise to the term $Q\chi_0^2$ in (82) of l.c. The latter term, except for proportionality factors independent of the character of the molecule, depends only on the total polarizability quite irrespective of the model. The same property is preserved when the calculations are adapted to translational fluctuations rather than the uniform spacing assumed in l.c., as the modification consists essentially in altering the value of Q . So Kirkwood's factor $-15/16$ is general.

³² With the general molecule, the leading term in λ equals $2kT\alpha^{(2)}V/\chi_0 P_0$ where $\alpha^{(2)}$ is defined as in Eq. (72) of l.c., provided $\alpha^{(2)}$ is calculated with a haphazard rather than uniform spacing of molecules. Cf. our footnote 3 and Eq. (82) of l.c.

³³ As far as the part due to the permanent moment is concerned, the present calculation shows considerable resemblance to that given by R. M. Fuoss in J. Am. Chem. Soc., **56**, 1031 (1934). However, we use a series development of the exponentials, whereas Fuoss had to resort to the method of steepest descents because he was interested in much higher concentrations (liquids) where the development would not be convergent.

element.) The partition function involves only even powers of E_0 , and we only need the approximation E_0^2 . In the expansion of the exponential functions, it is not necessary to consider products of the form $w_{ij}w_{jk}$ etc., when $k \neq i$, as such terms are easily seen to first contribute when $1/V^2$ rather than $1/V$ is considered in (19), the situation being similar to that for the second virial coefficient. Thus we may write

$$Z = \mathcal{J} \cdots \mathcal{J} [1 + \frac{1}{2} E_0^2 k^{-2} T^{-2} (\sum_i m_{zi}^2) [1 + \sum_{k>j} f_{jk}] \prod_i \exp(-b_i r_i^2 / 2kT) dv_i d\tau_i, \quad (23)$$

where

$$f_{ij} = -1 + \exp(-w_{ij}/kT). \quad (24)$$

Since the directions of r_{ij} are random, we may replace m_{zi}^2 by $\frac{1}{3} m_i^2$, and $m_{zi} m_{zj}$ by $\frac{1}{3} \mathbf{m}_i \cdot \mathbf{m}_j$. This can be demonstrated explicitly, for instance, by averaging over all directions for r_{ij} . On separating the terms for which l does, or does not equal i or j , and on performing the integration over the purely translational coordinates, Eq. (23) thus becomes

$$Z = (V - b')^L \Omega^L \left\{ [1 + \frac{1}{2} L^2 \mathcal{J} f_{ij} dv_{ij}] [1 + (E_0^2 / 6k^2 T^2) (L - 2) \mathcal{J} m_i^2 dv_{ij}] + (E_0^2 / 3k^2 T^2) \mathcal{J} \mathbf{m}_i^2 dv_{ij} + (L^2 E_0^2 / 12k^2 T^2) \mathcal{J} (\mathbf{m}_i + \mathbf{m}_j)^2 f_{ij} dv_{ij} \right\},$$

with the abbreviations

$$b' = 2\pi L a^3 / 3, \quad \Omega = \mathcal{J} \exp(-b_i r_i^2 / 2kT) dv_i, \quad dv_{ij} = \exp[-b_i (r_i^2 + r_j^2) / 2kT] dv_i dv_j / \Omega^2, \quad f_{ij} = (4\pi/V) \int_a^\infty f_{ij} r_{ij}^2 dr_{ij}.$$

In performing the translational integration, we have employed the conventional hard sphere model, with distance of closest approach a , and have neglected all but binary encounters. The various atoms are supposed alike in internal structure, so that subscripts do not really need to be attached to b_i , e_i , etc. As L is very large, it has been allowable to take the number of pairs of molecules as $\frac{1}{2} L^2$ rather than the more exact value $\frac{1}{2} L(L-1)$.

$$\mathcal{J} m_i^2 dv_{ij} = \mu^2 + 3\alpha kT \quad (\alpha = e_i^2 / b_i).$$

Here α is obviously the same as the usual coefficient of induced polarizability. The product of two integrals with integrands each involving f_{ij} can be disregarded, since their first contribution begins with $1/V^2$ in (19). Thus

$$Z/Z^0 = 1 + \frac{1}{2} E_0^2 L k^{-2} T^{-2} \left\{ (\frac{1}{3} \mu^2 + kT\alpha) (1 - L \mathcal{J} f_{ij} dv_{ij}) + \frac{1}{2} L \mathcal{J} \frac{1}{2} (\mathbf{m}_i + \mathbf{m}_j)^2 f_{ij} dv_{ij} \right\},$$

where Z^0 is the partition function in the absence of E_0 .

We now develop f_{ij} as an ascending series in w_{ij} . It is convenient to assume a spherically shaped containing vessel, since then the linear terms in w_{ij} make no contribution to Z . The latter is shown either by the general theory of l.c., or the obvious fact that with complete spherical symmetry, which demands a spherical boundary, the average values of the first and second parts of w_{ij} defined in (22) are equal. In this connection, however, we must remember that the field E_0 as we use it, is the external field before insertion of the body, and is the same as $E + 4\pi P/3$, where E is the field inside the spherical dielectric. The remarks of section 1 show that our final results will be independent of the shape of the body if they are expressed in terms of E rather than E_0 . Thus we find that if we stop with w_{ij}^4 and if we perform the spacial averaging over different relative inclinations of \mathbf{m}_i and \mathbf{m}_j

$$Z/Z^0 = 1 + \frac{1}{2} E_0^2 L k^{-2} T^{-2} \left\{ (\frac{1}{3} \mu^2 + kT\alpha) + \frac{1}{3} L \overline{r_{ij}^{-6}} k^{-2} T^{-2} \left[\frac{1}{3} \langle \mathbf{m}_i^4 \rangle_{AV} \langle \mathbf{m}_j^2 \rangle_{AV} - (\frac{1}{3} \mu^2 + \alpha kT) \langle \mathbf{m}_i^2 \rangle_{AV} \langle \mathbf{m}_j^2 \rangle_{AV} \right] + L(2/225) \overline{r_{ij}^{-8}} k^{-3} T^{-3} \langle \mathbf{m}_i^4 \rangle_{AV} \langle \mathbf{m}_j^4 \rangle_{AV} + L(1/75) \overline{r_{ij}^{-12}} k^{-4} T^{-4} [\langle \mathbf{m}_i^6 \rangle_{AV} \langle \mathbf{m}_j^4 \rangle_{AV} - \langle \mathbf{m}_i^4 \rangle_{AV} \langle \mathbf{m}_j^4 \rangle_{AV} (\mu^2 + 3\alpha kT)] + \cdots \right\},$$

where

$$\langle \mathbf{m}_i^n \rangle_{AV} = \Omega^{-1} \mathcal{J} \mathbf{m}_i^n \exp(-b_i r_i^2 / 2kT) dv_i.$$

Evaluation of the integrals gives

$$\langle m_i^4 \rangle_{AV} = \langle m_j^4 \rangle_{AV} = \mu^4 + 10\alpha\mu^2 kT + 15\alpha^2 k^2 T^2, \quad \langle m_i^6 \rangle_{AV} = \mu^6 + 21\alpha\mu^4 kT + 105\alpha^2 \mu^2 k^2 T^2 + 105\alpha^3 k^3 T^3, \\ \overline{r_{ij}^{-n}} = (4\pi/V) \int_a^\infty r^{-n+2} dr = [4\pi/V(n-3)] a^{-n+3}.$$

Eq. (20) finally follows on remembering that $P = kT \partial \log Z / \partial E_0$, and $\epsilon - 1 = 4\pi P / (E_0 - 4\pi P/3)$.

The writer wishes to thank Professors F. Simon and J. Stratton, and Dr. J. L. Oncley for valuable comments.